Bijay Karki

# Characterization of pulp and paper waste water samples using a prototype sensor (Langis Oy)

## Study on the corelation of COD with UV-abs and IR-abs.

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Usually online effluent water quality measurement systems are not incorporated in pulp and paper mills. Laboratory analyses are used to measure the parameters like suspended solids, Chemical Oxygen Demand, Biological Oxygen Demand ($BOD_5$), turbidity, pH and conductivity. The quality of the effluent can fluctuate between the timespan of sampling and getting the results. Hence, the real time monitoring and control of the effluent requires using online water quality sensors.

In this study, an online water quality sensor (prototype) was used to characterize the effluent from a Finnish pulp and paper mill. The sensor was manufactured by Langis Oy. The prototype was able to measure electrical conductivity, turbidity, total suspended solids, color and total dissolved solids from the given sample. Measurement of theses parameters was based on optical phenomenon except for the electrical conductivity.

Results showed that the waste water samples could not be characterized solely using the prototype. Laboratory experiments were performed in order to complete, compare and verify the prototype measurements. Infra-Red absorbance and conductivity measurement of the prototype was out of range; hence, recalibration and tuning was suggested to the manufacturer. Laboratory results shows conductivity, suspended solids and turbidity show good correlation among each other and help in estimating the level of chemical oxygen demand. Thus, the control system of the mill should be based on the online measurement of these parameters.

| | |
|---|---|
| Keywords | online water quality sensor, pulp and paper effluent, Langis Oy, optical measurement, correlation between water parameters |

**Preface**

This thesis is a study about an online water quality sensor (prototype) manufactured by Langis Oy. The study was proposed by Langis Oy and commissioned by Helsinki Metropolia University of Applied Sciences in a joint collaboration. The waste water samples required for the study were provided by a Finnish pulp and paper mill (anonymous). Commercial version of the prototype was used in the mill to monitor effluent water parameters.

Langis Oy manufactures wide range of cheap and easy to use water analysis sensors. The company specializes in measurements and solutions for water quality technology. They have been developing their products and technology in close collaboration with customers and research institutes. Two predecessor prototypes had been successfully tested in Helsinki Metropolia UAS prior to this study. This is a follow up study with the third generation prototype. The aim of this study is to characterize various waste water samples form the pulp and paper mill using the prototype.

I am extremely delighted and grateful to everyone who helped me during this study. I would like to show my immense gratitude to D.Sc. Erkki Räsänen for his enormous contribution and guidance in the technical details, experimental work and data analysis. Similarly, I would like to thank senior lecturer Kaj Lindedahl for his support and arranging an easy environment in the school and the lab for the study. I am indebted to Johanna Tikka and Kaisu Malmipuro for their assistance in the lab procedures and experimentations. I would also like to thank Dr. Minna Pannanen-Porkka for the academic guidance.

Finally, I would like to thank my family and friends for their support.

June 2016,
Bijay Karki

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## List of abbreviations

| | |
|---|---|
| AD | Analog to Digital |
| ADt | Air Dry tons |
| AOX | Adsorbable Organic Halogens |
| BAT | Best Available Technology |
| BOD | Biochemical (Biological) Oxygen Demand |
| CMOS | Complementary Metal Oxide Semiconductor |
| COD | Chemical Oxygen Demand |
| EC | Electrical Conductivity |
| HDMI | High-Definition Multimedia Interface |
| Hz | Hertz |
| IoT | Internet of Things |
| IPPC | Integrated Pollution Prevention and Control |
| IR | Infrared |
| IR-abs | Infrared absorbance |
| IR-sct | Infrared scattered |
| LED | Light Emitting Diode |
| N | Nitrogen |
| NTU | Nephelometric Turbidity Unit |
| P | Phosphorus |
| pH | potential Hydrogen |
| S | Siemens |
| SPI | Serial Pheripheral Interface |
| TDS | Total Dissolved Solids |
| TSS | Total Suspended Solids |
| USB | Universal Serial Bus |
| UV | Ultraviolet |
| UV-abs | Ultraviolet absorbance |
| V | Volts |

# 1 INTRODUCTION

Presence of liquid water on the surface of earth is the basis for all forms of life. In the present world, water serves mainly for domestic, agricultural and industrial use (UN-Water, 2014) . Though abundant, all the water present in the nature cannot be consumed directly. Even clean and good looking water might not be safe for consumption due to the presence of various contaminants and the health risk. Hence, the contaminants in the water like ions, minerals, chemicals and bacteria have to be treated before the intended consumption. The treatment improves the quality of the water and minimize the health risks associated. However, the treatment of water differs based on the quality required for the intended use. Drinking water requires the highest quality standards compared to the water required for the industrial or agricultural use according to the EU's Council Directive 98/83/EC on the quality of water intended for human consumption (Lenntech, 2016). The waste water produced after the consumption is also treated in waste water treatment facilities in order to release into the nature or to reuse.

It is vital to understand the parameters associated with the quality of water before, during and after any treatment. According to the Helsinki Region Environmental Services Authority (HSY, 2015), some parameters assessed for drinking water are alkalinity, fluoride, smell and taste, coliform bacteria, hardness, pH, iron, turbidity and electrical conductivity. Similarly, for the municipal waste water treatment, the Urban Waste Water Treatment Directive (UWWTD; 91/271/EEC) indicates the performance of any treatment plants is based on five different parameters namely biological oxygen demand (BOD), chemical oxygen demand (COD), total suspended solids (TSS), total Nitrogen (Ntot) and total Phosphorus (Ptot) (Eurpean Environment Agency, 2013).

In order to measure these parameters certain devices or tests are required. Lately water quality sensors are being used for this purpose. Due to the recent advancement in technologies like open-source and Internet of Things, these kinds of sensors are more economical, reliable and easy to use. Langis Oy is one of the companies manufacturing water quality sensors to meet low cost demand along with fulfilling the reliability and compatibility. And this thesis was executed to evaluate one of the prototypes manufactured by Langis.

Langis is a company which specializes in measurements and solutions for water quality technology. It was founded by Erkki Räsänen and Ari Kristol in 2012 in Espoo, Finland (Langis, 2016). The production facility is in Numminen, Finland. The company manufactures wide range of cheap, versatile and easy to use water analysis systems i.e. sensors, intended for water intensive industries like pulp and paper mills, waste water treatment plants and peat producers. (Langis, 2016). Products from Langis offer a combination of industrial and environmental measurement solutions with Internet of Things (IoT), data analysis and digitalized services. This versatile feature of the technology facilitates smart solutions for monitoring, control and automation.

Langis Oy has been developing their products and technology in close collaboration with customers and research institutions. This thesis was also commissioned by Langis in collaboration with one of their customers and Helsinki Metropolia University of Applied Sciences as a research institution.

The aims of this thesis were

- Characterization of waste water samples from the pulp and paper mill using the new prototype manufactured by Langis.
- Comparison of online results and lab measurements for reliability.
- Monitoring the performance and checking for any flaws in the prototype during the study period.

Similarly, a sub-question of thesis was, how does the COD correlate with UV-absorbance and IR-absorbance for a pulp and paper waste water sample?

# 2 THEORETICAL BACKGROUND

Sensor is a device which measures chemical or physical parameters from a given sample. Sensors can also indicate, record and respond to the measurement system depending on the design and flexibility. Water quality sensors are designed to measure parameters associated with water like pH, conductivity, turbidity and suspended solids. These sensors can be applicable for surface water, ground water and industrial water monitoring. The data provided by the sensors can be vital in understanding and protecting the water and environment from pollution.

The prototype used in this thesis can measure electrical conductivity, turbidity, total suspended solids, color and total dissolved solids in the given sample. These parameters are explained in the following chapters

## 2.1 Electrical Conductivity (EC)

The ability of water or any solution to allow the flow of electric current is known as electrical conductivity. The common unit of measurement is micro-Siemen per centimeter (µS/cm). EC is directly proportional to the concentration of the ions present in the medium. Hence, it can be measured to determine the concentration of salts or inorganic compounds like chlorides, alkalis and carbonates dissolved in the water. Conductivities of the different kind of water is presented in Table 1 (Lenntech, 2016). Total dissolved solids (TDS) can be calculated based on the measured EC. However, the relation varies based on the concentration of the sample (Lenntech, 2016).

*Table 1: Conductivities of different types of water*

| **Water** | **Conductivity** |
|---|---|
| Ultra-pure water | $5.5 * 10^{-6}$ S/m |
| Drinking water | 0.005 – 0.05 S/m |
| Sea water | 5 S/m |

Some important terms related to the measurement of the conductivity of any solutions are explained further,

Conductance is defined as the inverse of the electrical resistance (R) created by the solution between the electrodes. It is represented by the letter G.

$$G = \frac{1}{R} \text{ (Siemens)}$$

Cell constant is defined as the ratio of the distance (d) between the electrodes to the area (a) of the electrodes (Radiometer analytical, 2014).

$$K = \frac{d}{a}$$

where $K$ = cell constant ($cm^{-1}$)

$a$ = effective area of the electrodes ($cm^2$)

$d$ = distance between the electrodes (cm)

## 2.2 Total Dissolved Solids (TDS)

Any salts, minerals, metals, cations and anions which are dissolved in water are known as dissolved solids. Total dissolved solids refer to the combined inorganic and some fraction of organic matter dissolved in water (Oram, 2014). The unit of measurement is milligram per liter (mg/l). As discussed in the previous chapter, TDS and EC can be compared for dilute solution. TDS can also be roughly estimated based on EC using the following relationship (Lenntech, 2016),

TDS (mg/l) = 0.5 x EC (dS/m or mmho/cm) or

= 0.5 * 1000 x EC (mS/cm)

Similarly, for concentrated solutions where TDS is greater than 1000 mg/l and EC is greater than 2000 mS/cm, the relationship shifts as follows;

TDS (mg/l) = 0.9 x EC (dS/m or mmho/cm)

And for agricultural and irrigation water, the relationship can be expressed as follows:

TDS (mg/l) = 640 x EC (dS/m or mmho/cm)

Hardness, scale formation, taste (bitter or salty) and corrosive properties of the water are due to the TDS (Oram, 2014). These properties are based on the types of cations and anions dissolved in the water.

## 2.3 Turbidity

Turbidity is a measure of the clarity or the degree of loss of transparency of water due to the suspended particulates (Lenntech, 2016). Turbidity is expressed in Nephelometric Turbidity Unit (NTU), Formazin Nephelometric Unit (FNU) and Formazin Turbidity Unit (FTU). It is one of the important parameters to estimate the quality of the water. According to World Health Organization (WHO) turbidity of drinking water should be below 1 NTU in ideal cases and should not exceed 5 NTU. Hence, the lower turbidity, the better the quality of the water. Various factors affecting the turbidity are humic acid, dyes, bacteria, clay, algae, slit, decaying plants and animals, settable and non-settable solids. Turbidity also gives some estimation about the total suspended solids (TSS) in the sample.

In this thesis, HI 88713 ISO Turbidimeter and the prototype was used to measure the turbidity from the given samples and the results were processed in NTUs.

## 2.4 Total Suspended Solids (TSS)

Suspended or colloid particles which are extremely small and cannot be settled by gravity are commonly referred as total suspended solids. It can also be referred as the particles which cannot pass thorough a fine filter of pore size 0.45 micron (µm) from a settled water sample (Oram, 2014). The unit of measurement of TSS is milligram per liter (mg/l). Mathematically,

$$TSS\left(\frac{mg}{l}\right) = \frac{(m2-m1)*1000}{V}$$

where

*m1* = initial mass of the filter paper (in gram)
*m2* = final mass of the filter paper (in gram)
*V* = volume of the water sample (in liter)

## 2.5 Chemical Oxygen Demand (COD)

Chemical Oxygen Demand (COD) is the total amount of the oxygen required to chemically oxidize the pollutants (organic and inorganic) present in the given sample of water. The unit of COD measurement is milligram per liters (mg/l). COD consists of the biodegradable organic matter (BOD) and other oxygen demanding materials. COD is also used as an indirect measurement to indicate the amount of contaminants present in any given sample of water (Karki, 2016).

Conventionally COD is measured by determining the left over oxidizing agent such as dichromate or permanganate which are used in excess. This procedure takes couple of hours to complete the analysis and the chemicals used during the analysis possess health issues and safety concerns (Latif & Dickert, 2014). Therefore, various sensors have been designed for quick estimation and determination the COD of a given water sample.

## 2.6 Biochemical Oxygen Demand (BOD)

Biochemical Oxygen Demand (BOD) is also known as biological oxygen demand. It is the amount of oxygen consumed by the microorganisms to decompose the biodegradable materials present in the water bodies. The unit of BOD measurement is milligrams per liters (mg/l). The major cause for the BOD are biodegradable organic carbon and ammonia present in the water. The sources of these compounds are domestic and industrial waste including byproducts of plants and animals (YSI, 2016).

Five-day BOD ($BOD_5$) is the standardized test used to determine the BOD. $BOD_5$ is the amount of oxygen consumed over 5 days of incubation period under specified standard conditions. Depending on the nature of the water and the national regulations, $BOD_7$ is also used. $BOD_7$ is the amount of oxygen consumed in 7 days' period (European Environment Agency, 2015). For comparison $BOD_7$ can also be converted to $BOD_5$ using the relation $BOD_7 = 1.16\ BOD_5$. It is one of the important water quality parameters in determining the performance of any water treatment facility.

Measurement of BOD is a time consuming practice which also requires experience and skill to achieve reproducible results. To overcome this problem, alternative methods to

estimate the BOD using biosensors also have been explored and reported (Kim, et al., 2003) (Preininger, et al., 1994) .

## 2.7 Spectrophotometry

Spectrophotometry is the study of the interaction between matter and the light. The National Institute of Standards and Technology (The National Institute of Standards and Technology, 2015) defines spectrophotometry as the quantitative measurement of the reflection or transmission properties of a material as a function of wavelength. This method is used to measure the absorbance or transmittance by measuring the intensity of the light beam passing through a sample. Concentration of a substance in the given sample can also be determined using this technique. Moreover, unknown contaminants in the water can also be determined using this technique. This is a crucial finding in many applications from drinking water to environmental safety and protection (Katrina, 2015).

The devices used in the spectrophotometric analysis is called spectrophotometer. It consists of a spectrometer and a photometer. The spectrometer emits light of desired color or wave length while the photometer detects and measures the intensity of the light. The instruments are arranged in such a way that a liquid or solid sample in a cuvette lies in between the spectrometer and the photometer. Hence the amount of light passing through the cuvette is measured by the photometer (Anon., 2015). Basic structure of the spectrophotometer is illustrated in Figure 1 (Anon., 2016).

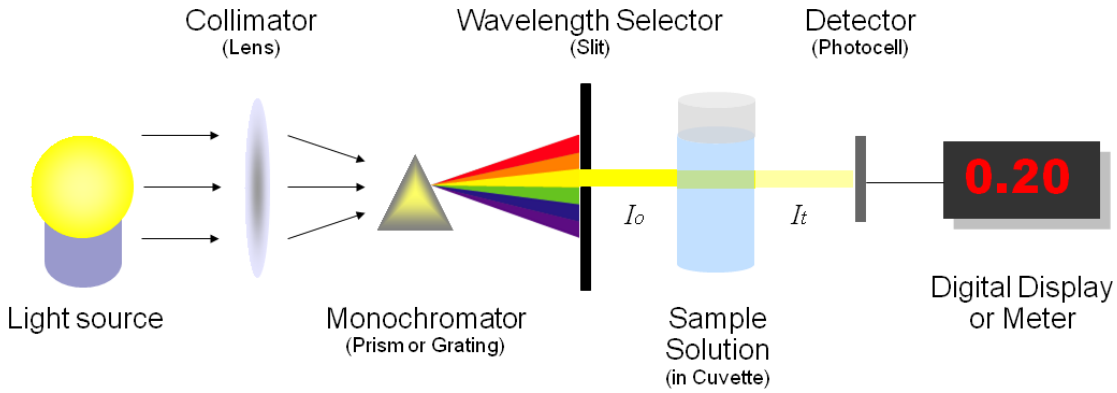



*Figure 1: Basic structure of a spectrophotometer*

### 2.7.1 Transmittance

For solid samples, the term transmittance is used in spectrophotometric analysis. It is the ratio between the intensities of light measured with and without the sample (Shimadzu Corporation, 2016).

Mathematically it can be expressed as,

$$T = \frac{It}{Io}$$

where $T$ = transmittance

$I_t$ = light intensity with a sample

$I_o$ = light intensity without a sample

### 2.7.2 Absorbance

For liquid samples the term absorbance is commonly used in spectrophotometric analysis. It is the amount of the light absorbed by the sample solution. It is the logarithmic function of transmittance (Shimadzu Corporation, 2016).

Mathematically, absorbance can be expressed as follows;

$$Abs = Log_{10}\frac{1}{T}$$

where $T$ = transmittance

$Abs$ = absorbance

### 2.7.3 Lambert-Beer law

Lambert-Beer law is the linear relationship between absorbance and concentration of an absorbing species (Shimadzu Corporation, 2016). For a monochromatic light, the absorbance is directly proportional to

- the concentration of the solution
- the length of the light path (cuvette)

Mathematically, the Lamber-Beer law can be written as follows;

$$Abs = Log_{10}\frac{1}{T} = \varepsilon cl$$

where $\varepsilon$ = molar absorptivity coefficient (wavelength dependent)
$c$ = concentration of the sample
$l$ = length of the light path (cuvette)

Limitations of the Beer-Lambert law

In the real practice the linearity of the Lambert-Beer law is not valid under certain circumstances. The deviations seen in the Lambert-Beer law are of three kinds (Mehta, 2012):

a) Real deviations

These deviations are seen at high concentrations (>0.01M) due to electrostatic interactions between molecules. The high analyte concentration can change the refractive index (η) of the solution. The problem with change in refractive index can be corrected by slight modification in the Lambert-Beer law:

$$\text{i.e. } Abs = \varepsilon cl\ (\eta^2+2)^2$$

b) Chemical Deviations

These deviations arise due to the certain chemical phenomenon of the analyte molecule like association, dissociation and interaction with the solvent. All these phenomena directly affect the absorption spectrum.

c) Instrument Deviations

These deviations are observed as a result of some common source of errors like mismatched cuvettes, presence of interfering light and most importantly use of polychromatic source of radiation to create monochromatic beam. To minimize the deviations in absorption, measurements are taken at wavelength of maximum absorbance.

### 2.7.4 Brown color

Color in water is the result of humus, plankton, weeds, industrial waste, peat materials and metallic ions. Natural occurrence of living and decaying organic particles in water exhibits yellowish or brownish color (Christman & Ghassemi, 1966). Hence the brown color is dependent upon the organic materials present in the water. However similar color

pattern can be created by the industrial effluent even with different constituents. With proper methods and tools, it is possible to establish a relation between COD and the brown color. Several studies confirmed that peat water samples show very strong correlation between brown color and COD. UV is the complement for brown color. UV also attenuates with brown color. This is because COD absorbs brown light and brown light relates with UV.

# 3 PULP AND PAPER MILL (WASTE WATER)

Effluent from one of the pulp and paper mills in Finland was used in this study. The mill produces book papers, improved newsprint grades, magazine papers and business papers. In the European Union, environmental permit system for major industrial installations like pulp and paper mills are governed by the Integrated Pollution Prevention and Control (IPPC, 96/61/EC, codified version 2008/1/EC) directive. The IPPC promotes best available techniques (BATs) among the industrial installations for pollution control technologies, efficient resource and energy consumption as well as prevention of accidents and disturbances.

Pulp and paper industries generate waste water discharges, atmospheric emissions and noise pollution. Since the prototype used in this study can measure only water parameters the focus is in water discharges. A study done for Finnish pulp and paper mills suggests the major parameters evaluated in the waste water discharges of are $BOD_7$ (kg/ADt), $COD_{Cr}$ (kg/ADt), TSS (kg/ADt), P (kg/ADt), N (kg/ADt) and the flow rate ($m^3$/ADt) (Silvo, et al., 2009). ADt is the air dry tons of pulp product where the weight of the pulp product is corrected to reflect the weight that the pulp product would be if the pulp were composed of 10% water and 90% fiber (Queen's Printer BC, 1990). AOX is halogenated organic compounds that are adsorbable by activated carbon. Waste water discharges from paper mills usually do not cover monitoring of AOX even though it is often mentioned. The waste water emissions of Finnish mills are shown in Figure 2.

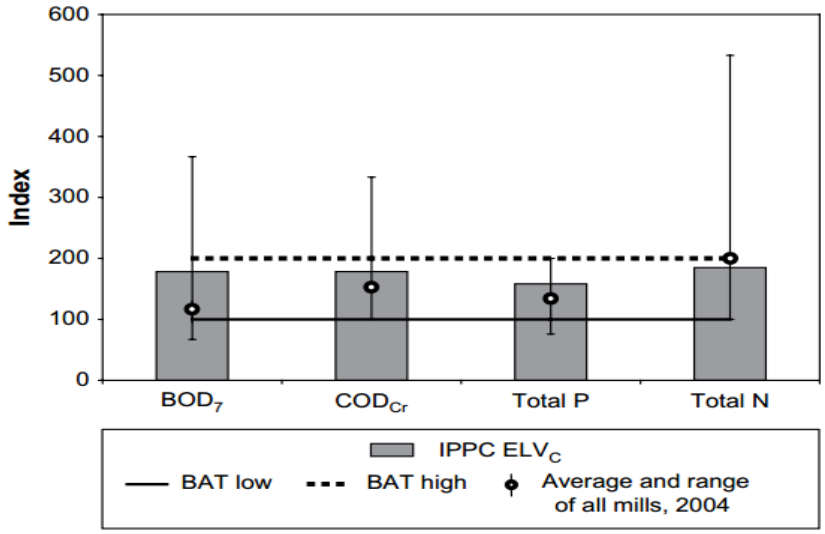



*Figure 2: Emissions from Finnish paper and board mills (Silvo, et al., 2009)*

# 4 PROTOTYPE

Among several water quality sensors developed by Lanigs Oy, 3rd generation prototype was used in this study. The working platform of the prototype was Raspberry Pi 2, Model B V1.1 with “Raspbian GNU/Linux 8 (jessie)” operating system. The Raspberry Pi is a cheap and very small sized computer which plugs into a screen via HDMI port and uses a standard keyboard and mouse via USB (Raspberry Pi Foundation, 2016). It works like a normal computer. It is also capable of doing things like browsing the internet, playing high-definition video, making spreadsheets, word-processing, and playing games. The codes required to operate the prototype was programmed in Python Programming Language. And the codes can be found in Appendix 9.

The prototype was complied with the IEC 60529 Ingress Protection Rating of IP68 so it was protected against total dust ingress and was suitable for long term immersion to water (DSM&T, 2016). The prototype operated in five volts (5 V). It measured electrical conductivity, turbidity, total suspended solids, color and total dissolved solids from the given sample. The prototype was programmed such a way that the parameters mentioned were measured in every three seconds. According to Langis Oy frequency of the measurement could be as high as 80 Hz but only 3 Hz was used. It was a combination of several optical sensors to measure parameters based on absorbance and or scattering of the light. Except for the electrical conductivity all other measurements were based on optical readings. All the optical signals were converted into electric signals i.e. voltage and the voltage was converted into digital signals into bits. During the operation of the prototype there was a real-time graph of the readings taken by every sensor. Besides, a data file in “.CSV” format was automatically created on the background when the prototype was operational. A picture of the prototype and a schematic is shown in Figure 3 and Figure 4 respectively. The measurement principles of the various parameters and the application in sensor are explained in the following chapters.

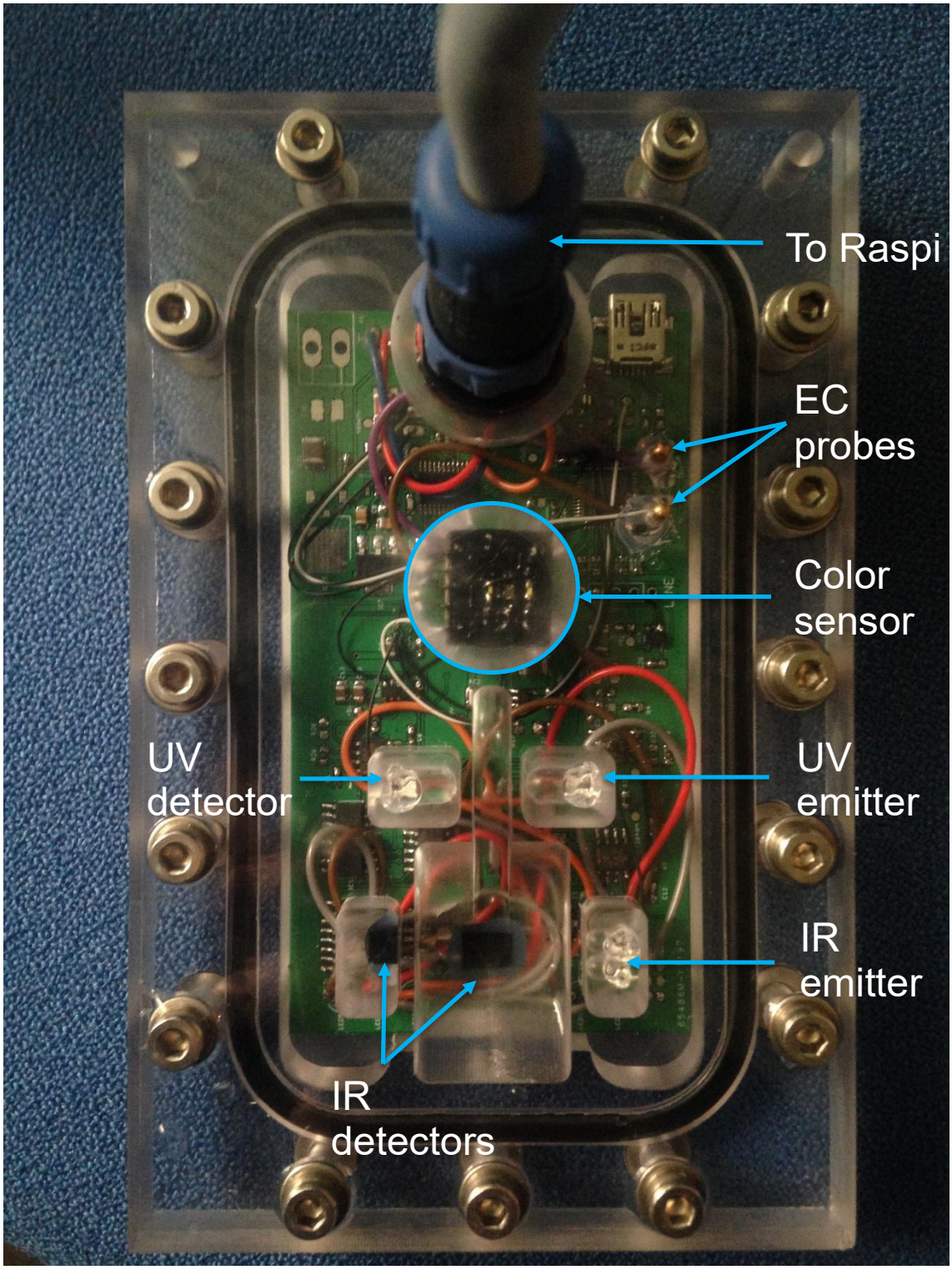



*Figure 3: Prototype with basic labels*

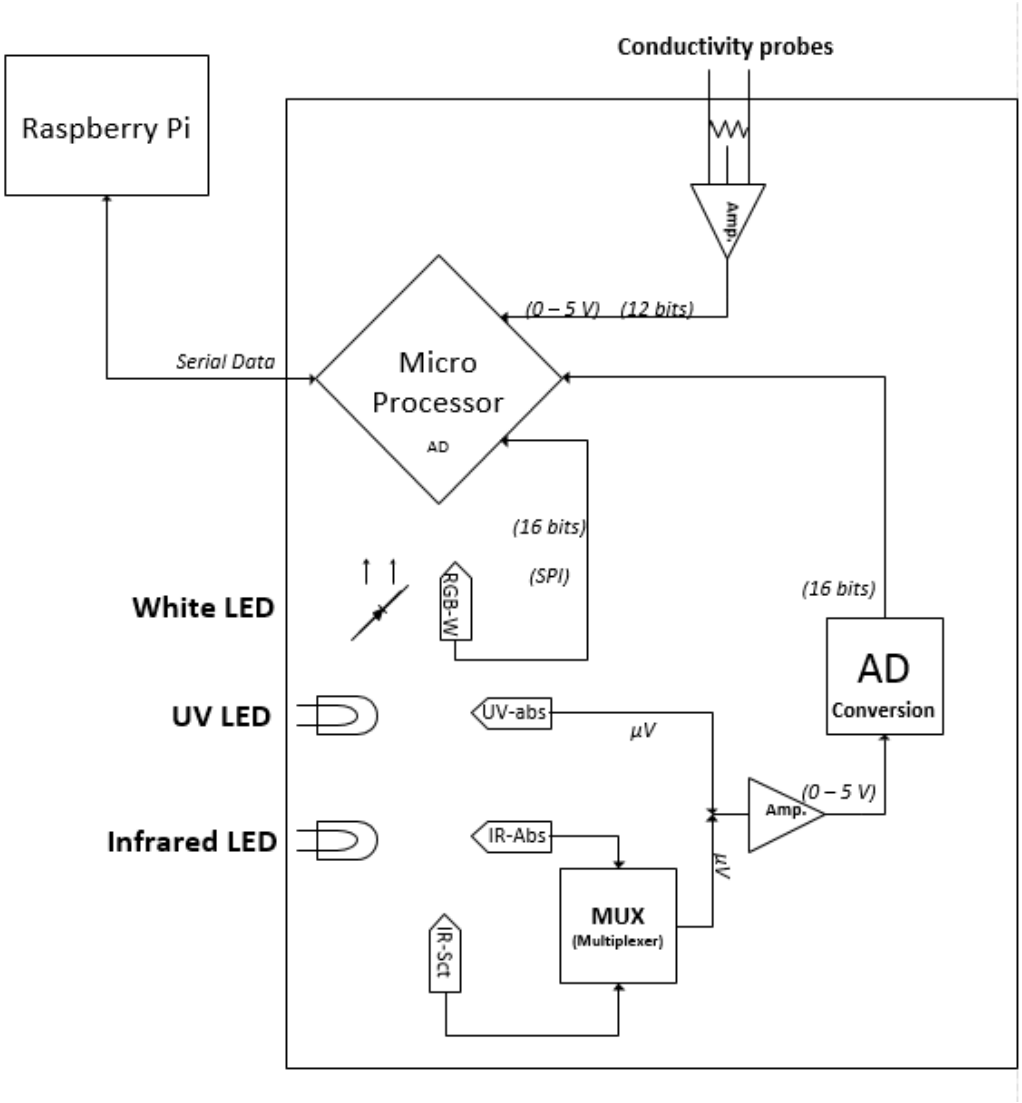



*Figure 4: Schematic of the prototype*

## 4.1 Electrical Conductivity (EC) measurement

Conductivity is measured by applying alternating current of certain frequency to the electrodes immersed in the solution and measuring the potential difference (voltage) across them. Generally, the frequency of the current is regulated by the meter, low frequencies are applied at low conductivities and vice versa. Direct current is not used due to the risk of electroplating or wearing down of the electrodes. A general circuit diagram for a conductivity meter is shown in the Figure 5 (Radiometer analytical, 2014). The meter then generates the value of conductivity based on the conductance and the cell constant. Mathematically, this could be expressed as follows;

$$k = G \times K$$

where $\kappa$ = conductivity (S/cm)

$G$ = conductance (S), where G = 1/R

$K$ = cell constant ($cm^{-1}$)

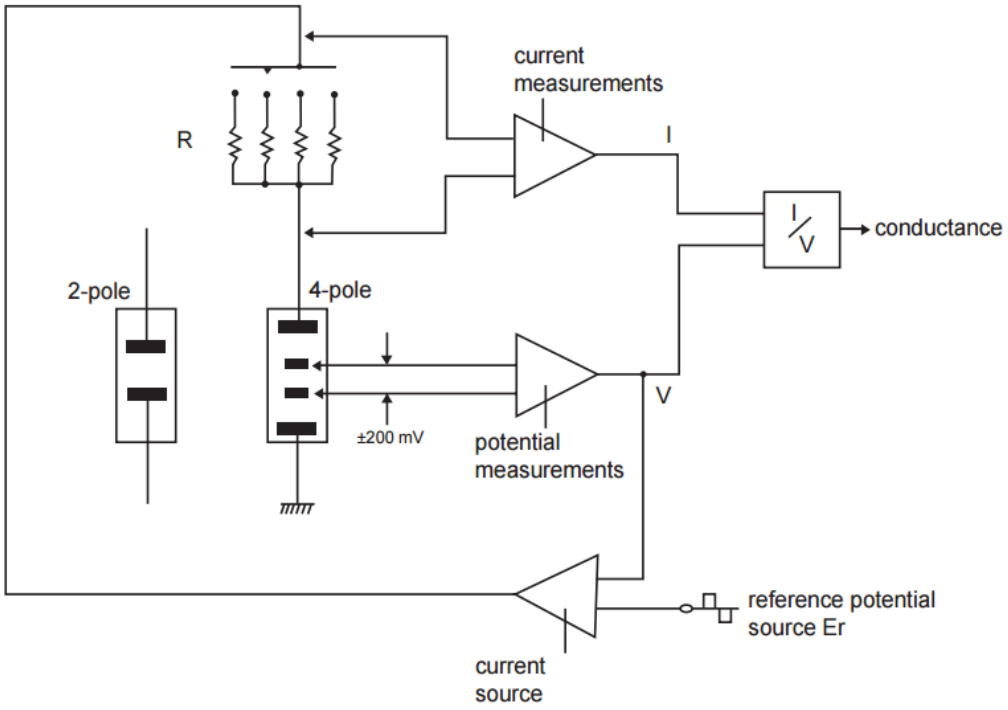



*Figure 5: General circuit diagram of a conductivity meter*

The prototype had two small protruding electrodes to measure the electrical conductivity of the water samples. It had two pole mechanism instead of four pole as shown in Figure 5. The electrodes measured the potential difference across the water sample. Then the electrical signal generated was amplified to the scale between zero to five volts. The signal was further digitized by the microprocessor of the prototype into 12 bits.

## 4.2 Ultraviolet (UV) measurement

The prototype was equipped with two UV LEDs. One of them was designed to emit the ultraviolet radiation while the other as a UV light detecting sensor. The LED produced UV radiation of wavelength 405 nm. The light then passes through the sample. The sensor then produced electrical signals in microvolts (µV) based on the intensity of the light received. The signals were then amplified to the scale between zero to five volts (V) by an amplifier. Finally, the amplified electrical signal was digitized by an AD converter into 16 bits digital signal and forwarded to the microprocessor of the prototype.

### 4.2.1 Ultraviolet Absorbance (UV abs)

Measuring brown color of the sample was based on the absorption of the ultraviolet light. There was a valley in the prototype acting as a light path where the sample could sip inside and hold on in between the LED and the sensor. The length of the light path was five millimeters (5 mm). UV light was not emitted constantly but once in every three seconds. Hence, UV abs was also measured in every three seconds. A circuit diagram for UV measurement is shown in Figure 6.

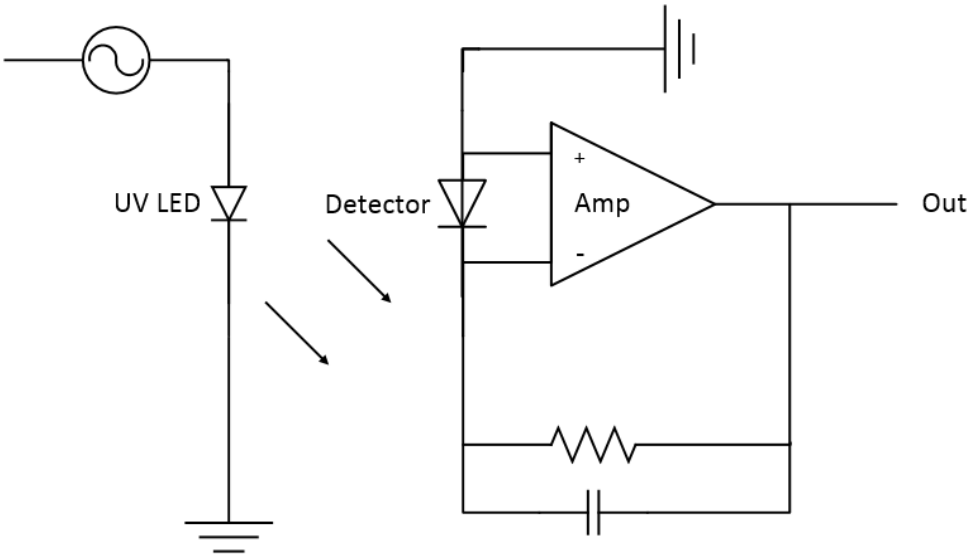



*Figure 6: Circuit diagram of UV LED and the detector*

It was also discovered that UV detecting sensor emitted light. The differences between the LEDs were in the intensity of the lights emitted and the application. During the experimentation as visible to the naked eyes, emission of a bright blue light from the first LED was followed by a faint blue light from the detecting LED. The detecting LED emitted light in order to measure the junction temperature. In general, the junction temperature is the temperature of a device or a circuit during the given operational conditions (Cypress Semiconductor, 2015). The junction temperature of the LED was measured to compensate the interference due to the ambient temperature because the UV measurement is temperature dependent. The working mechanism of the detecting LED is shown in Figure 7. After measuring the UV absorbance small current is passed through the detector LED which emitted a very faint blue light. The signal was amplified and the junction temperature was measured in order to compensate the interference. Sometimes the junction

temperature can be very high inducing thermal runoff effect which then breaks down the equipment. So the heat has to be taken away from the diode or the equipment.

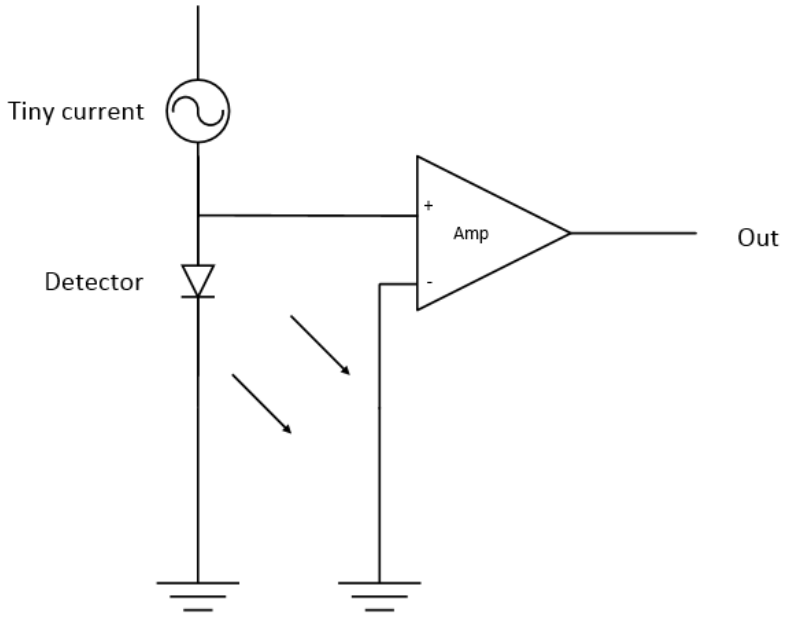



*Figure 7: Circuit diagram for junction temperature measurement*

## 4.3 Infrared (IR) measurement

Measurement of the total suspended solids (TSS) and the turbidity was based on the absorption and scattering of the infrared light. For this purpose, the prototype was equipped with a LED and two sensors detecting infrared as shown in Figure 8 (Dahal, 2016), almost the same working mechanism like the UV mentioned in the previous chapter. The LED emitted infrared radiation of wavelength 1100 nm. The light then passes through the sample. The light path was twenty millimeters (20 mm). The sensors then produced electrical signals in microvolts (µV) based on the intensity of the light received. Signals from both sensors travelled in the same line via a multiplexer. The electricals signals were then amplified between zero to five volts (V) by an amplifier. Finally, the amplified electrical signal was digitized by an AD converter into 16 bits digital signal and forwarded to the microprocessor of the prototype.

Unlike the UV LEDs, the light emitted by the infrared LED was not visible to the naked eyes. Similarly, the light path for IR measurement was wider and bigger compared to the UV measurement.

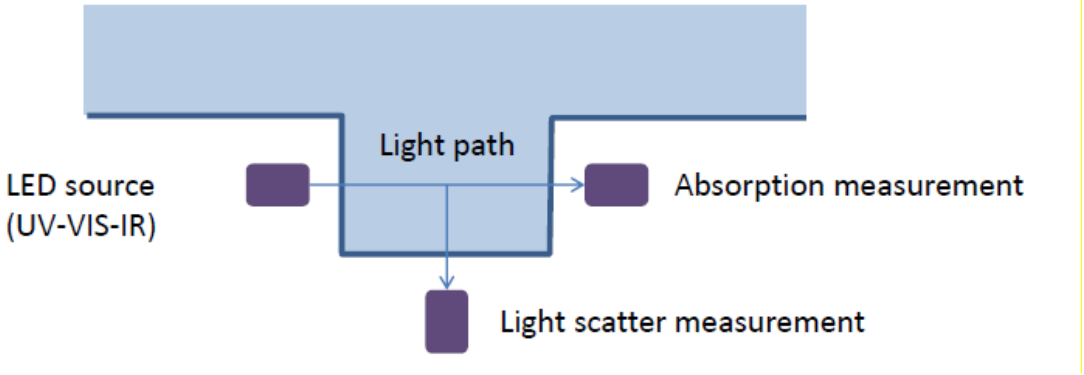



*Figure 8: Working mechanism of absorption and scattering of light*

### 4.3.1 Infrared Absorbance (IR-abs)

The sensor located at an angle of 180 degrees with respect to the infrared LED was used to measure the infrared absorbance. This sensor measured the intensity or the amount of the infrared radiation absorbed by the particles present in the water sample. This measurement was used to estimate the total suspended solids present in the given water sample based on the fact that infrared absorbance is directly proportional to the suspended solids.

### 4.3.2 Infrared Scattered (IR-sct)

The sensors which was at an angle of 90 degrees with respect to the infrared LED was used to measure the scattered infrared. It measured the intensity or the amount of the infrared scattered by the undissolved particles at 90-degree angle. This is a general principle used to determine the turbidity of a given water sample. But it is extremely important to consider the scattering of the light caused by the suspended particles varies with the shape, size, refractive index and composition of the particles (Crittenden, et al., 2012).7

## 4.4 Color

The prototype was able to detect red, green, blue and white lights from the water samples. In order to detect these colors VEML6040 color sensor was used in the prototype. The color sensor consists of photo diodes, amplifiers and analog/digital circuits put together into a single chip using CMOS (Complementary metal-oxide-semiconductor) process (Vishay Semiconductors, 2015). The dimension of the sensor is 2.0 mm (length) x 1.25 mm (width) x 1.0 mm (height). Though not directly related to this study but the most important applications of this sensor is in digital photography.

The sensor works on the phenomenon of back scattering of the white light. At first a LED emits white light, projects to the samples and the back scattered light were again picked up by the sensor. The sensor generates 16 bits of digital data at a time and is directly sent to the microprocessor of the prototype via SPI (Serial Peripheral Interface) bus connection. According to the manufacturer the peak sensitivities of the sensor for red, green and blue light are at 645 nm, 575 nm, and 460 nm respectively as included in Appendix 3 (Vishay Semiconductors, 2015). Colors were not investigated in details; however, the correlation between blue and brown color was studied.

# 5 MATERIALS AND METHODS

A list of the equipment used during the study is shown in .

Table 2.

*Table 2: General equipment used for experiments and measurements*

| Equipment | Type | Application |
|---|---|---|
| Prototype (sensor) | Langis Oy (3rd generation) | Characterization of pulp and paper waste water sample |
| Spectrophotometers | HACH LANGE (DR 3900) | Measuring COD concentration of samples |
| | UV/Visible (Ultrospec 2000) | Measuring absorbance of samples at 405 nm and finding absorbance peak value in UV/ VIS region |
| | Shimadzu (UV-160) | |
| Heater | HACH LANGE (LT 200) | Heating the cuvettes with samples |
| Turbidity meter | HI 88713 ISO Turbidimeter | Turbidity measurement |
| Conductivity meter | Mettler-Teldo AG | Conductivity measurement |
| Analytical balance | Mettler (AE240) | Weighing the filter paper |
| Chemical kit | HACH LANGE (LCK 514) | COD analysis |
| Oven | Memmert | Drying the filter papers |
| Glass wares | Beakers, graduated cylinder, pressure filtration setup | Filtration, dilution, |
| Pipette | Automated | Sampling small volume (> 5 ml) |
| Fridge | Normal | Sample storage |
| Lab safety gears | Normal | Personal protection |

## 5.1 Samples

Samples required for this study were provide by a Finnish pulp and paper mill. All together five dispatch of waste water samples were delivered by the company to Metropolia UAS. Each dispatch included five samples with a total of 22 samples from different dates. Volume of the samples from each dates was approximately one liter. The samples

were stored in the fridge. The first dispatch was delivered when the mill was undergoing scheduled cleaning and maintenance. Hence those samples were not analyzed.

### 5.1.1 Dilution

Dilution of the samples were performed based on the interest of Langis Oy which was in 1:2 ratios for each consecutive sample. All together six dilution series were prepared out of a sample as shown in Table 3.

*Table 3: Dilution series*

| Dilution series | Concentra-tion | Volume of sample | Total volume |
|---|---|---|---|
| 1 | 100 % | 800 ml | 800 ml |
| 2 | 50 % | 400 ml | 800 ml |
| 3 | 25 % | 200 ml | 800 ml |
| 4 | 12.5 % | 100 ml | 800 ml |
| 5 | 6.25 % | 50 ml | 800 ml |
| 6 | 0 % | 0 ml | 800 ml |

The following equipment were used for the dilution of the sample:

- 1000 ml beakers
- Graduated cylinder (500 ml)

A minimum of 800 ml of the sample in a beaker was required to immerse the prototype and its sensors. Hence 800 ml was chosen as a standard volume for the analysis. Dilution series were prepared one after another from the mother solution but not all together at once because of the limited volume of the sample. Ion exchanged water and normal tap water were used in order to dilute the original sample. The dilution series prepared for turbidity measurement is shown in Figure 9.

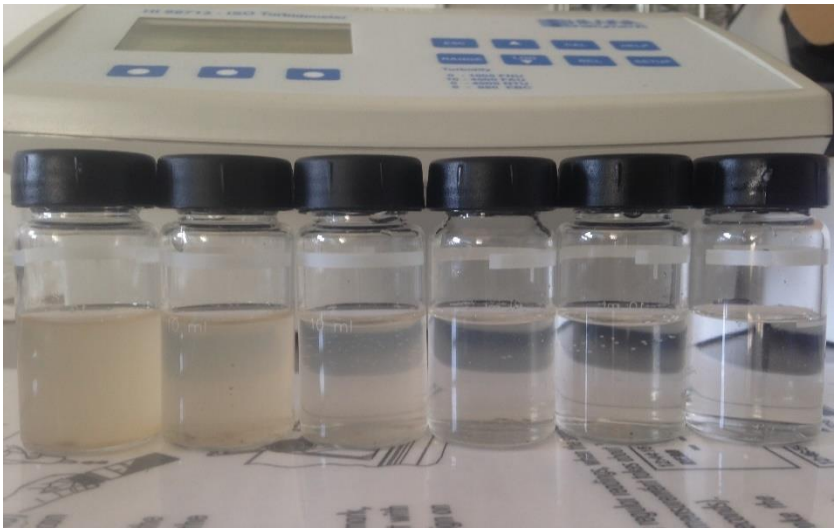


*Figure 9: Dilution series in decreasing order of concentration*

## 5.2 Online setup

All the experimentations using the prototype was performed in the lab. The dilution series of samples prepared as mentioned in the previous chapter were analyzed. The actual online setup was quite simple. First of all, the prototype was connected to the power and the computer program required to operate the prototype was launched in the Raspi. A brief operational instruction of the prototype is also included in the Appendix 1. 800 ml of samples were then taken in one-liter beaker and the prototype was immersed in the beaker as shown in Figure 10. Several graph plots were observed in the screen in response to the measurement taken. The data were retrieved for further processing and analysis after completing the experimentation.

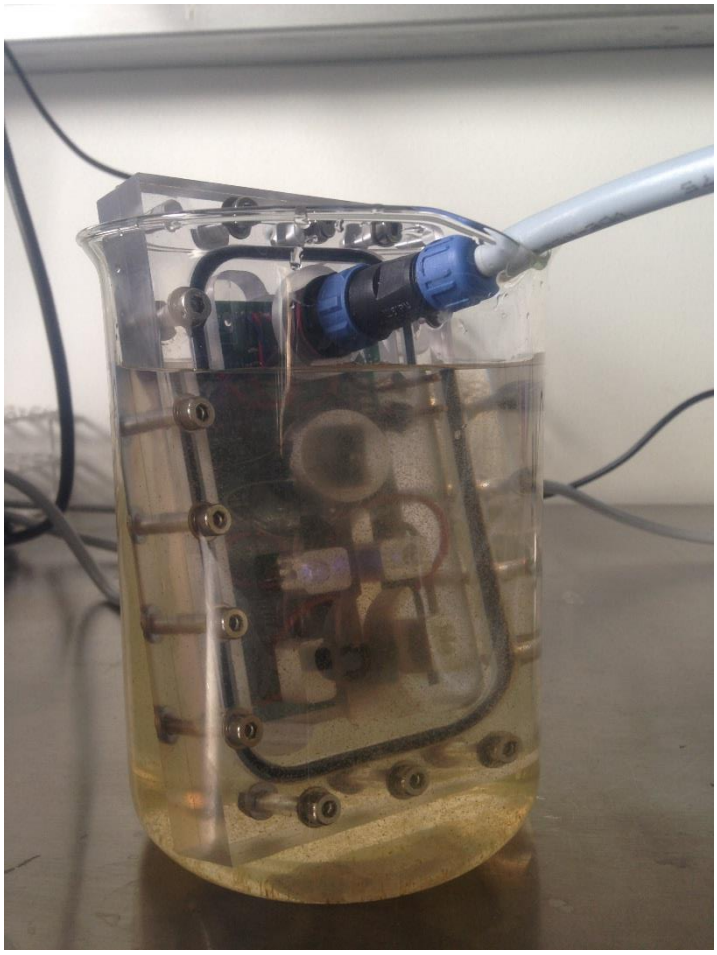


*Figure 10: Online setup of the prototype*

## 5.3 Lab experiments

All the experimentations mentioned in this chapter were carried out in the laboratory of Metropolia UAS. Personal and environmental safety was put on the top priority hence lab protocols were strictly followed. Lab engineers were also consulted for any kind of doubts and confusions. Experimentation performed using the lab instruments are discussed in the following sub-chapters.

### 5.3.1 Total Suspended solids

Pressure filtration method was used to determine the amount of the suspended solids from a sample.

#### *5.3.1.1 Equipment Required*

A list of the equipment used during the study to determine the suspended solids is presented below:

i. Millipore filter papers (0.45 µm)
ii. Flask
iii. Funnel
iv. Vacuum pump (tap water)
v. Metal clamp
vi. Tweezer
vii. Crucibles
viii. Desiccator
ix. Analytical beam balance
x. Graduated cylinders

#### *5.3.1.2 Procedure*

In the beginning samples were diluted to 50 % concentration using ion exchanged water and the mass of the filter paper was weighed. Then the filtration apparatus was setup. The filter paper was placed on the filter head and a funnel on top of the paper. A metal clamp was used to attach and hold the filter head and the funnel together. After the apparatus was secured, a pump (vacuum suction through running tap water) was connected.

The diluted sample was then poured into the funnel and pumping was started. When the filtration was over the apparatus was disassembled. The filter paper was removed using a tweezer and transferred to a crucible. The crucible was then placed into an oven at 103$^{o}$ C for drying. After approximately one hour, the crucible was taken out of the oven. The filter paper was then placed in a desiccator to cool down in a moisture free environment for about half an hour.

After cooling down, the filter paper was again weighed using an analytical beam balance. The mass of the filter paper before and after the filtration were recorded to calculate the amount of suspended solids in the given sample (**Error! Reference source not found.**).

### 5.3.2 Turbidity

HI 88713 ISO Turbidimeter was used to determine the turbidity in the samples. Measurement principle of this device was similar to the prototype i.e. based on the scattering of the infrared light at 90-degree angle. The device was capable of measuring turbidity of the following ranges,

- 0 - 1000 FNU (Formazin Nephelometric Units)
- 10 - 4000 FAU (Formazin Attenuation Units)
- 0 - 4000 NTU (Nephelometric Turbidity Units)
- 0 – 980 EBC (European Brewery Convention)

A list of the equipment used to as follow;

i. HI 88713 ISO Turbidimeter
ii. 10 ml pipette and pipetteerballon
iii. Cuvettes

#### *5.3.2.1 Procedures*

At first the device was calibrated according to the instructions provided by the manufacturer, HANNA instruments. Samples from each dilution series were analyzed. The standard volume of samples required was 10 ml and special cuvettes provided with the turbidimeter. Hence a pipette was used for the précised volume in the cuvettes. The measurements were taken and recorded when the samples from each dilution series was ready.

### 5.3.3 Electrical conductivity

Electrical conductivity (EC) of the sample were determined using the following equipment,

i. Mettler-Teldo AG conductivity meter
ii. Ion exchanged water

#### *5.3.3.1 Procedure*

The conductivity meter was calibrated according to the instructions provided before the experimentation. This involved the use of a standard solution having conductivity of 3.17 µS/cm. The probe of the meter was properly rinsed with the ion exchanged water before taking any measurements. Data from each measurement was recorded.

### 5.3.4 Chemical Oxygen Demand (COD) analysis

In order to determine the COD level in the samples readymade chemical kit LCK 514, (COD cuvette test) of the range 100-2000 mg/l $O_2$ from HACH Lange was used. This test kit is based on dichromate method with ISO 6060-1989, DIN 38409-H41-H44 standard (HACH LANGE, 2015). Quality certificate with the technical data for cuvette test LCK 514 is also included in Appendix 8. According to the suggestion and interest of Langis Oy, COD of the filtered samples were analyzed rather than the original samples. Following equipment were used for the COD analysis,

i. Spectrophotometer (DR 3900)
ii. Heater (HACH LANGE (LT 200)
iii. LCK 514 cuvette
iv. Cuvette holder
v. Automated pipette
vi. Pipette tip (0 - 5 ml)

#### *5.3.4.1 Procedure*

This test was performed with great alert compared to any other experimentation during this study. The LCK 514 kit was labelled as corrosive and toxic. Hence the safety data sheet was assessed before the experimentation (HACH LANGE, 2005). The risk and the

safety statements associated with the chemicals in the test kits are presented in Table 4.

*Table 4: Risk and Safety statements of LCK 514 COD Cuvettes*

| R phrases | S phrases |
|---|---|
| 33,35,45,46,60,61,23/24/25,42/43,52/53 | 53,26,45,36/37/39 |

Standard procedure set by HACH LANGE was followed to determine the COD of the given sample. At first the sediment in the cuvette was brought into suspension by inverting a few times. The lid was opened and 2 ml of sample was added into the cuvette using an automated pipette. The lid was put back and the cuvette was inverted once again. After cleaning from outside the cuvette was placed into a thermostat heater for two hours at 148 °C. When the digestion was completed the hot cuvette was removed carefully and invert twice. Then the cuvette was allowed to cool to room temperature. Evaluation was carried out when the sediment was completely settled down. The cuvette was cleaned from the outside and evaluated in the spectrophotometer (DR 3900). The barcodes in the cuvette made the measurement in the spectrophotometer automated. The kit was handled and stored properly during and after the experiment.

### 5.3.5 Spectrophotometric analysis

Shimadzu (UV-160) UV-Visible Recording and UV/Visible (Ultrospec 2000) spectrophotometers were used in this study. The basic difference between these two spectrophotometers were in the number of light beams used. Shimadzu had two light beams, each for reference and the sample. While Ultrospec 2000 had only one light beam. Similarly, Shimadzu (UV-160) could analyze only three sample at a time but Ultrospec 2000 could analyze five at a time. Moreover, Ultrospec 2000 was computer operated, easy to use and newer version than Shimadzu. Hence, Ultrospec was used more often than Shimadzu but this decision was not based on the performance or the accuracy of these instruments. The main aim of using these instruments were,

- Scanning the samples in whole UV and VIS region to detect the absorbance peaks
- Determining absorbance of the samples at a specific wavelength

Initially Shimadzu spectrophotometer was used to analyze few samples for the peak absorbance values in the whole ultraviolet and visible region. Absorbance at the specific wavelength of 405 nm for the samples were also analyzed. Ion exchanged water was taken as the reference.

Ultrospec was used later in the experimentation to do the same task but mostly for the filtered samples. All together 13 filtered samples were analyzed using the same technique. Dilution series of a milk sample were also analyzed using this spectrophotometer.

# 6 RESULTS

Parameters observed during this study were based on the interest of the pulp and paper mill and the application of the prototype. This chapter consists of the major findings from the laboratory analysis and the measurements using the prototype in order to characterize the effluent from the pulp and paper mill.

## 6.1 Laboratory Analysis

Results produced from the lab analysis are included in this chapter. All together 22 samples starting from the date 22.02.2016 till 29.03.2016 were analyzed. Four different parameters, TSS, COD, turbidity and EC were measured for each sample. The corresponding data table is included in Appendix 4.

### 6.1.1 Total suspended solids (TSS)

Two replicates from each samples were prepared for the laboratory measurement of the TSS. The result shown in Figure 11 is the average value of two replicated measurements.

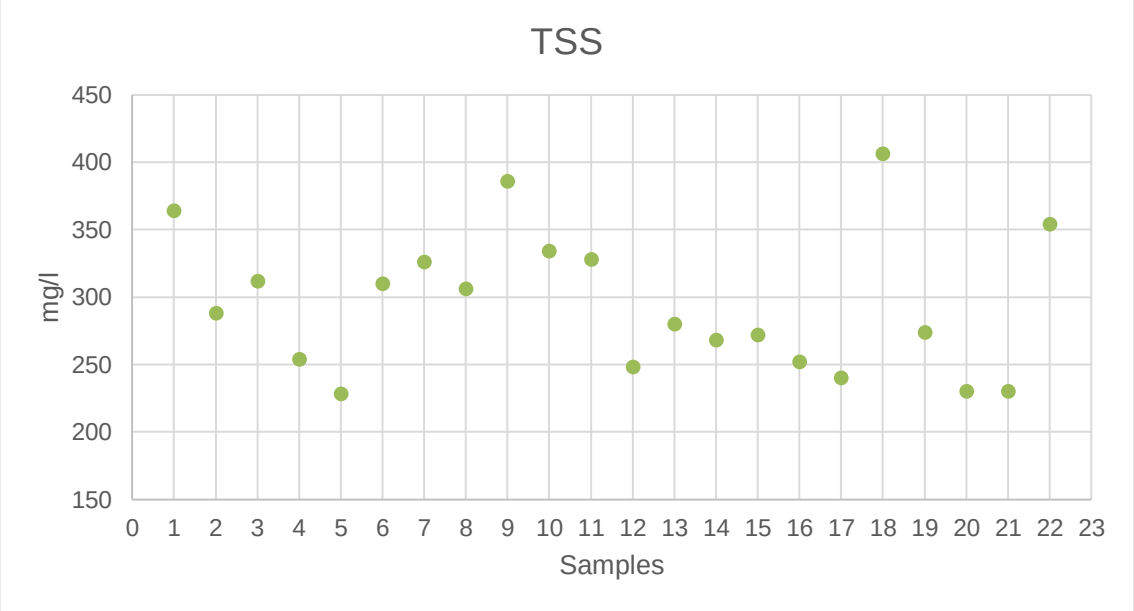



*Figure 11: Laboratory measurement of TSS*

### 6.1.2 COD Analysis

COD for each samples were analyzed using the LCK 514 chemical kit in two replicates. The average COD level of the samples is shown in Figure 12.

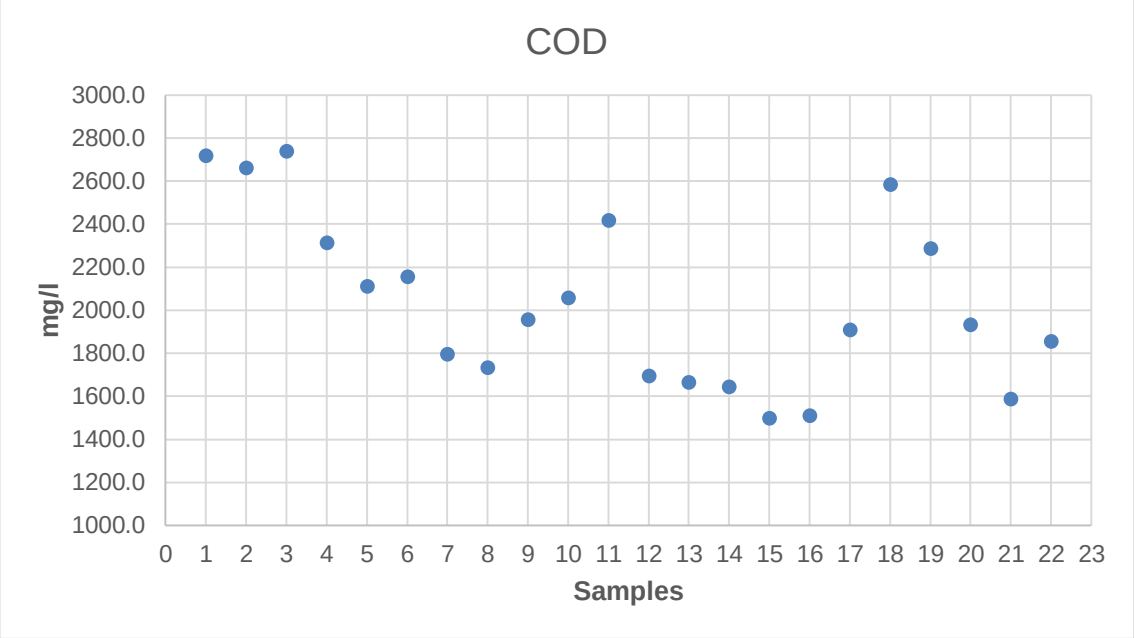



*Figure 12: Laboratory analysis of COD*

### 6.1.3 Turbidity

Figure 13shows the turbidity of each samples. The result is the average value of two replicated measurements.

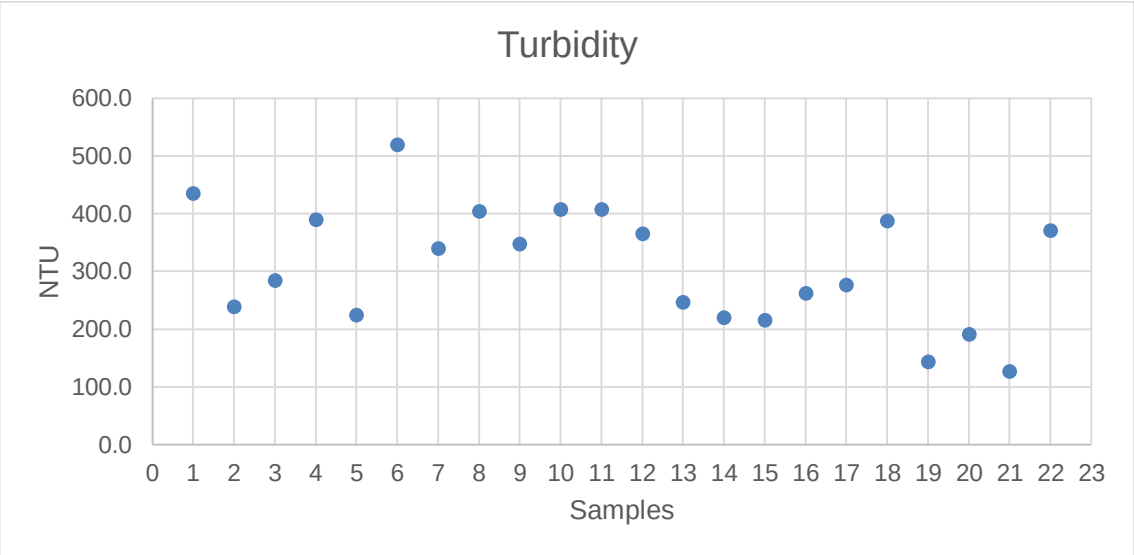



*Figure 13: Laboratory measurement of Turbidity*

### 6.1.4 Electrical Conductivity

Figure 14 shows the electrical conductivity of each samples. Like all other parameters the result for EC is also the average value of two replicated measurements.

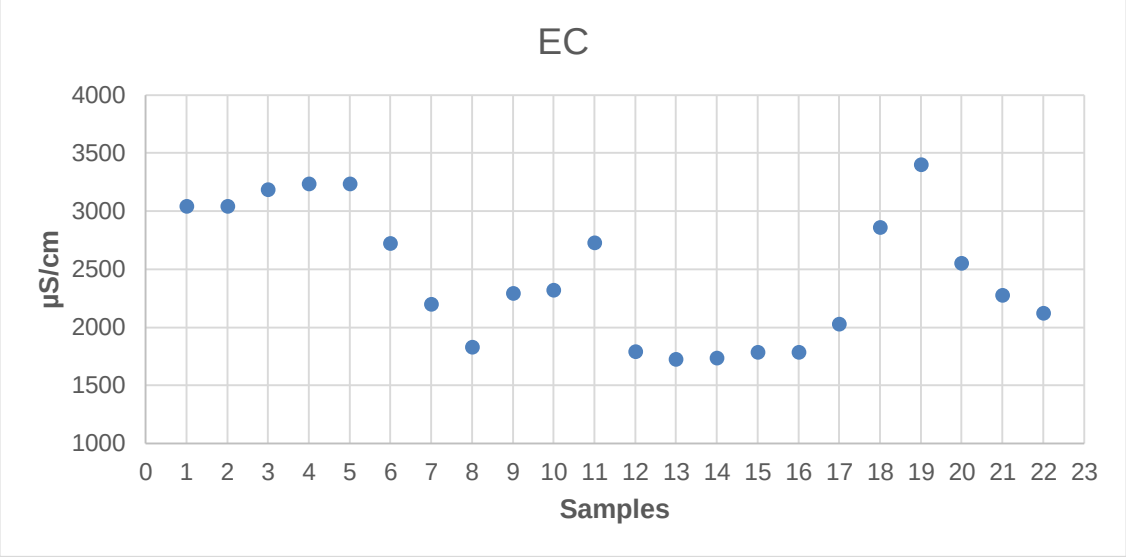



*Figure 14: Laboratory conductivity measurement*

## 6.2 Prototype measurement

This chapter consists of the results produced by the prototype. The prototype produced the measurement results as a graphical plot and a file with the actual data points. An example of the online graphical plot of a dilution series is included in Appendix 2.

Like the previous chapter, the same 22 samples starting from the date 22.02.2016 till 29.03.2016 were measured simultaneously using the prototype and the results are presented in following graphs. Instead of making the replicated measurements the dilution series of each samples were measured using the prototype. Vertical axes in all the graphs are in bytes while the horizontal axes correspond to the sample dates in numerical order. The corresponding data table is included in Appendix 5.

### 6.2.1 UV Absorbance

UV radiation absorbed by each samples (100 % concentrated) is shown in Figure 15. The result is the average value of the repetitive measurements taken by the prototype during the sample analysis.

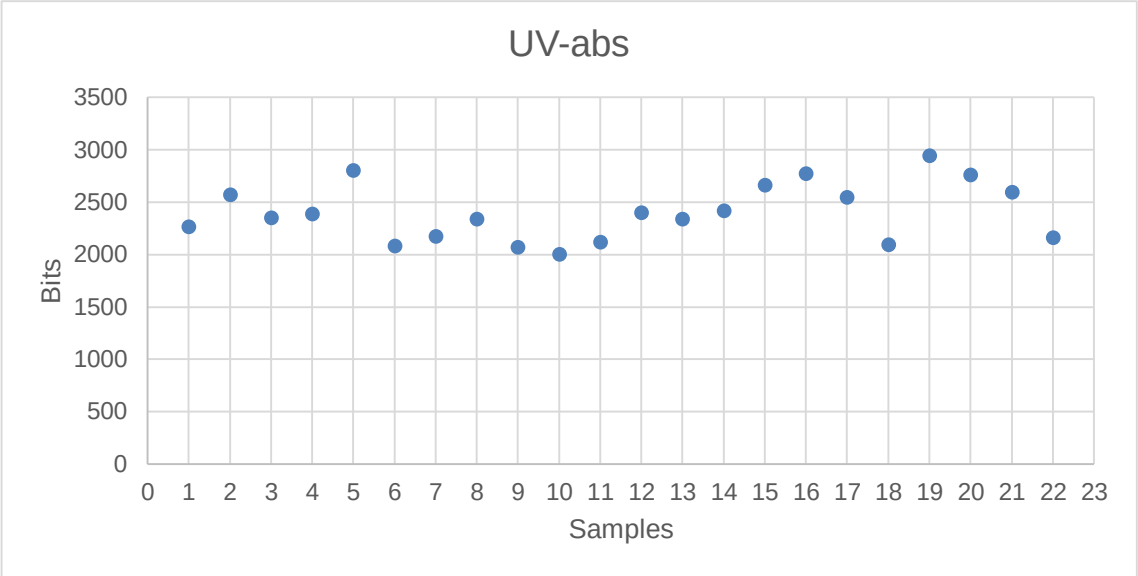



*Figure 15: Measurement of UV absorbance using the prototype*

### 6.2.2 Infrared (IR) scattered

IR radiation scattered by the particles in each samples (100 % concentrated) is shown in Figure 16. The result is the average value of the repetitive measurements taken by the prototype during the sample analysis

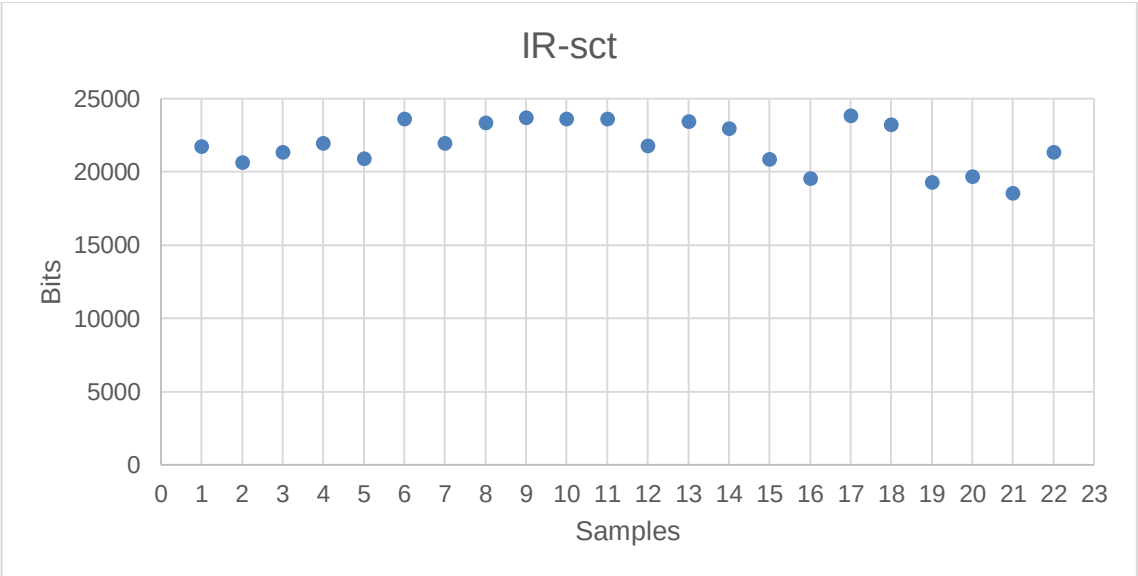



*Figure 16: Measurement of IR scattered using the prototype*

### 6.2.3 Infrared Absorbance

IR absorbed by the particles in each samples (100 % concentrated) is shown in Figure 17. The result is the average value of the repetitive measurements taken by the prototype during the sample analysis.

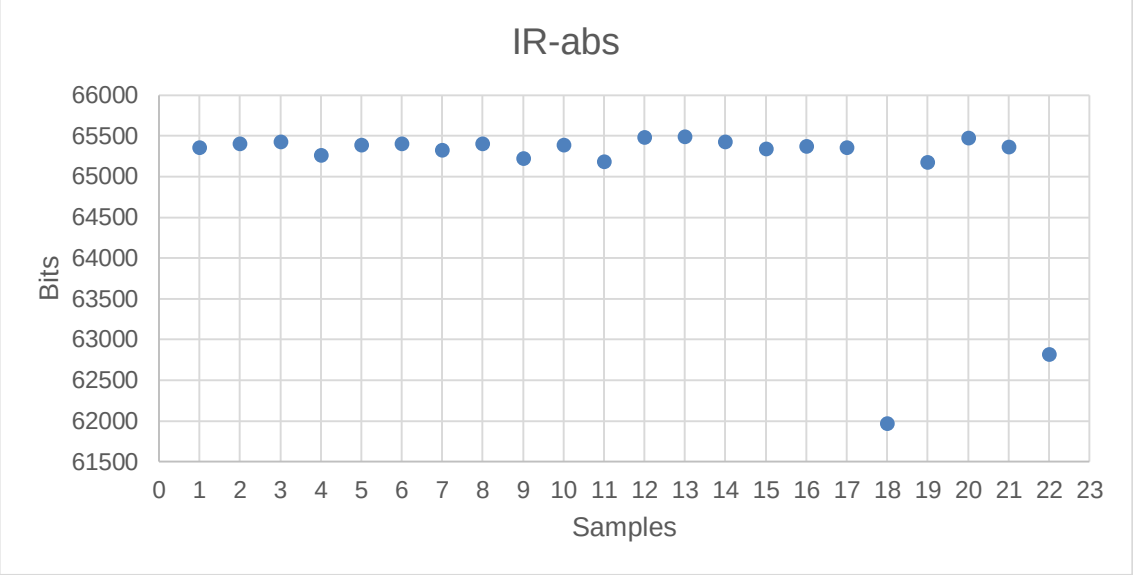



*Figure 17: Measurement of IR absorbance using the prototype*

### 6.2.4 Conductivity

Measurement of EC of each samples (100 % concentrated) is shown in Figure 18. The result is the average value of the repetitive measurements taken by the prototype during the sample analysis.

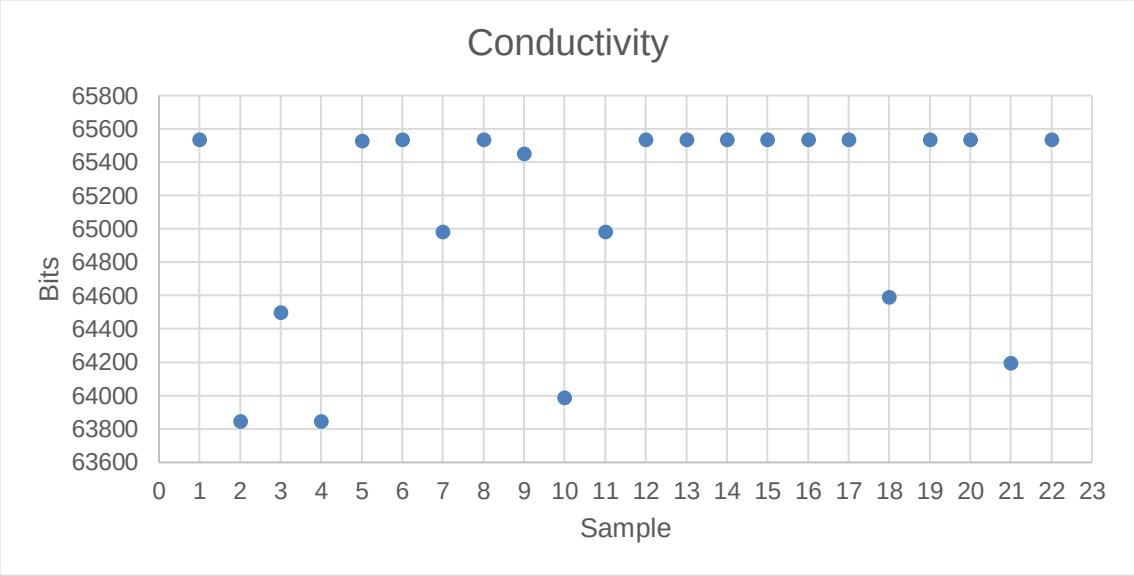



*Figure 18: Conductivity measurement using the prototype*

### 6.2.5 RGBW

Measurement of the color of each samples (100 % concentrated) is shown in Figure 19. Four different colors, red (R), green (G), blue (B) and white (W) were measured by the prototype. The corresponding results of each samples are put together in the same graph. The result is the average value of the repetitive measurements taken by the prototype during the sample analysis.

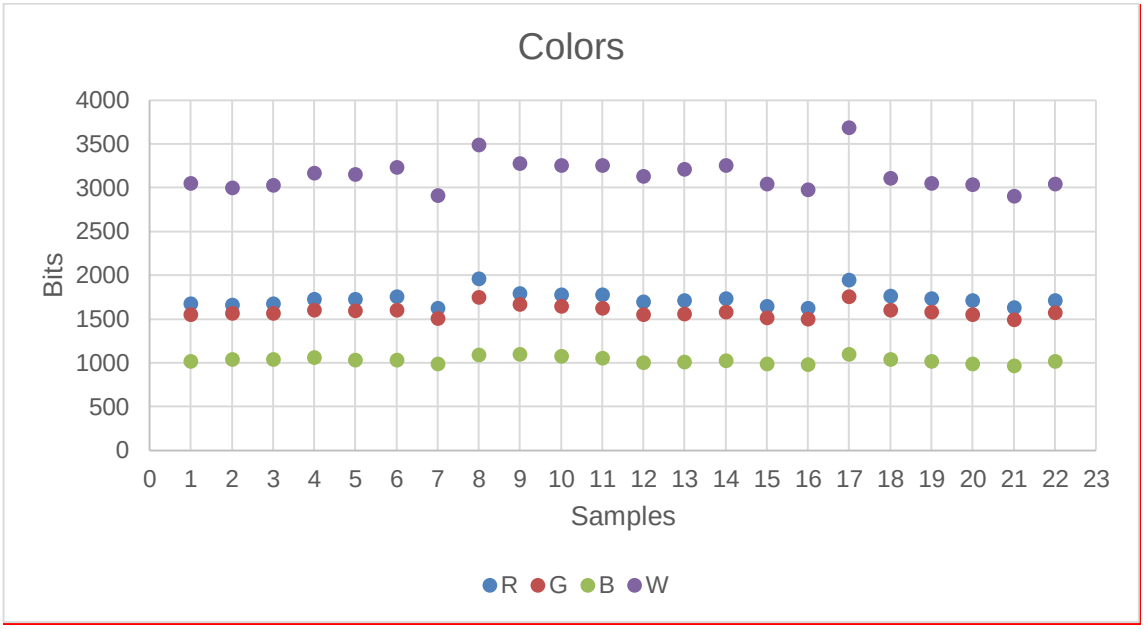



*Figure 19: Color measurement using the prototype*

# 7 ANALYSIS AND DISCUSSION

In this chapter the results are further analyzed to check and establish relation between the parameters measured during the study.

## 7.1 Laboratory results

The normalized over view of the parameters measured in the laboratory as shown in Figure 20 indicated EC and COD have strong correlation. Similarly, some correlation is observed between TSS and turbidity. The points are connected with a solid line for easy visual detection of correlation.

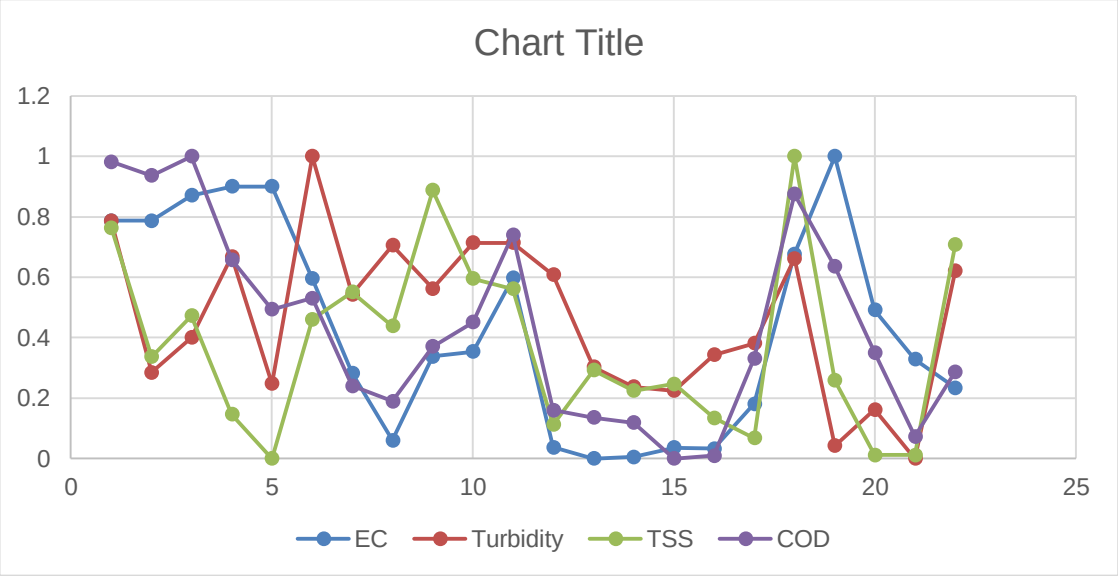



*Figure 20: Normalized overview of the laboratory measurement*

The graph shown in Figure 21 confirms there is a strong correlation between electrical conductivity and COD.

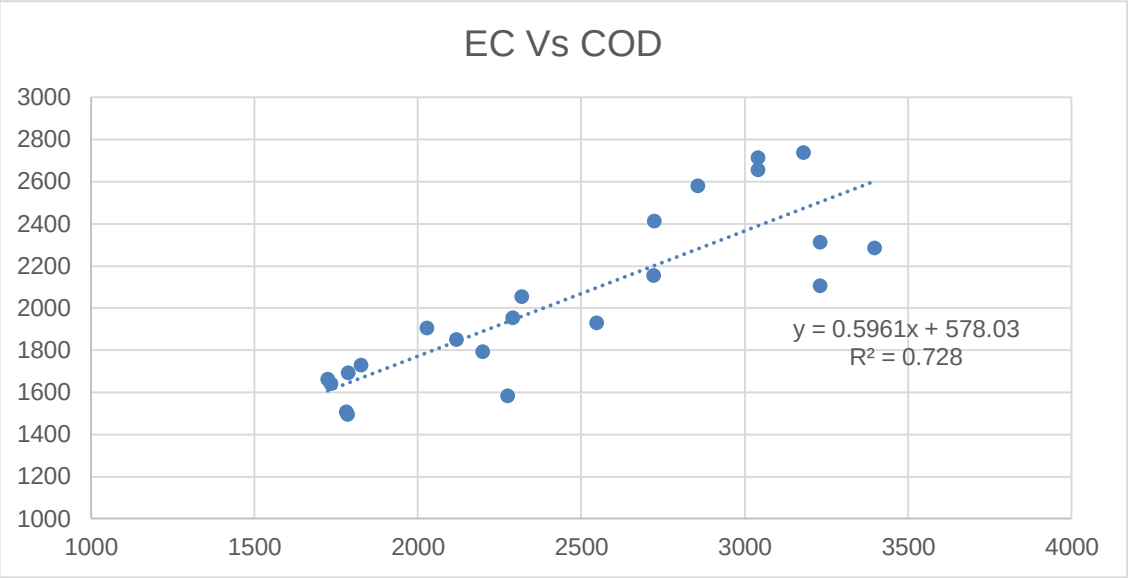



*Figure 21: Correlation between EC and COD*

Similarly, the graph shown in Figure 22 confirms there is a nice correlation between TSS and turbidity though not as strong as between EC and COD.

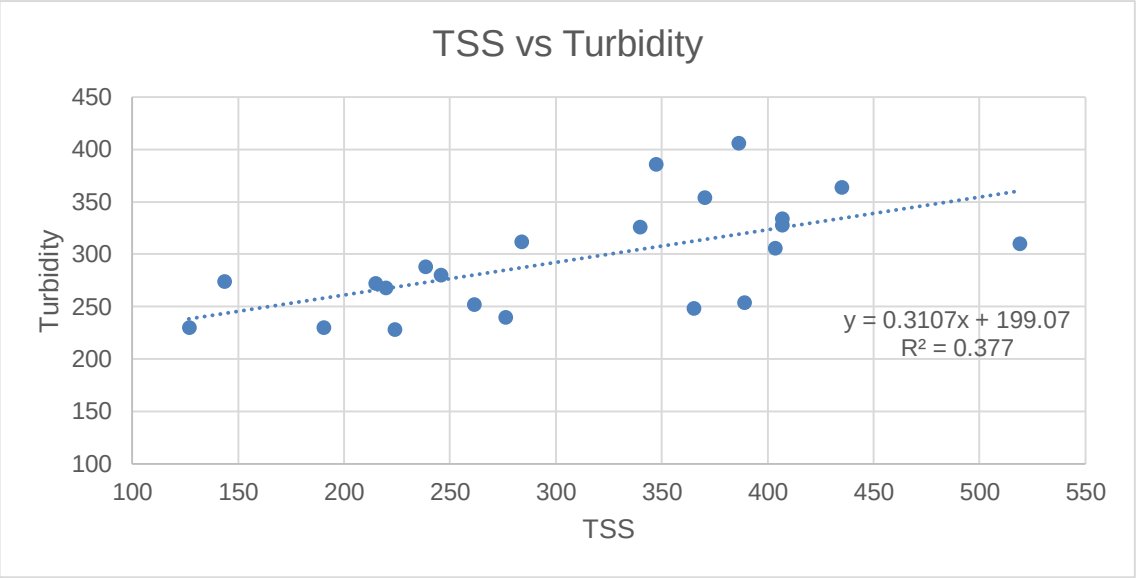



*Figure 22: Correlation between TSS and Turbidity*

These observations are also valid with the existing knowledge that turbidity is used for approximation of TSS (in addition to IR abs) and conductivity is sometimes used for COD estimation (Räsänen, 2015).

## 7.2 Prototype measurement

Response of the prototype was assessed by the calibration curve method at various dilution for each sample. Out of 22 samples only one sample from the date 01.03.2016 was chosen to be discussed in this chapter. The choice of this particular sample was a random selection.

The UV absorbance measurements show a nice linear fit with respect to each dilutions of the sample. The corresponding UV absorbance measurement is shown in Figure 23.

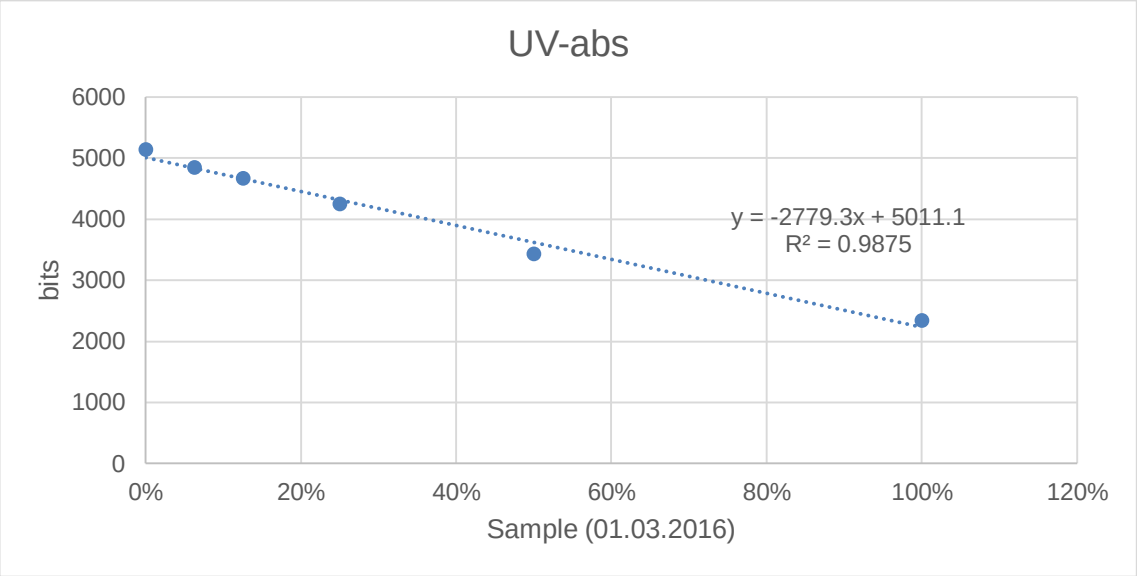



*Figure 23: UV-abs measurement of a dilution series*

The IR scattered measurements also show a nice linear fit with the dilution series of the sample. The corresponding IR scattered measurement is shown in Figure 24.

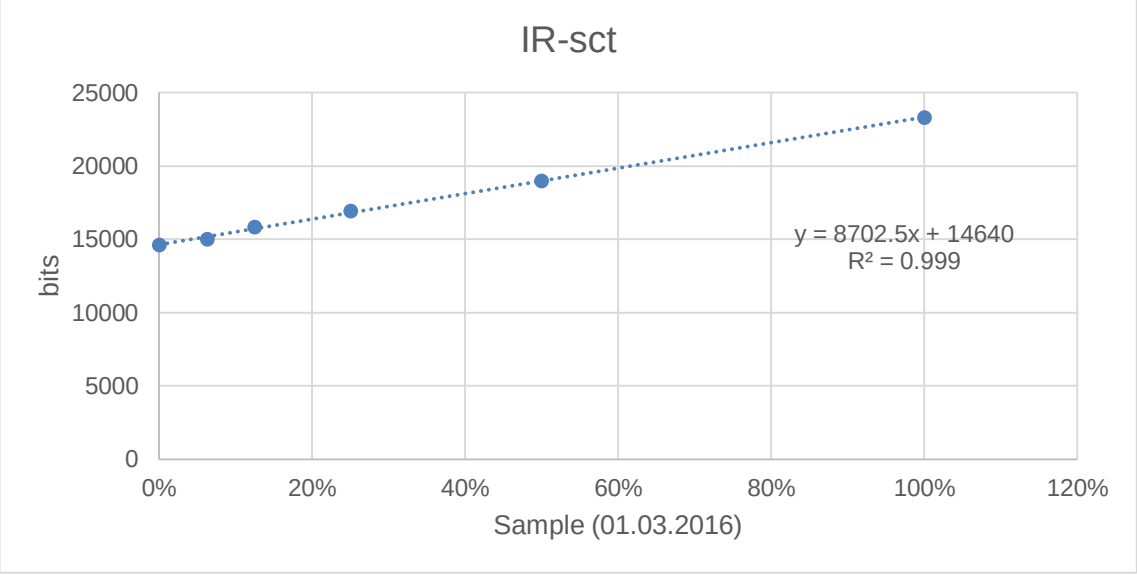



*Figure 24: IR-sct measurement of a dilution series*

Unlike UV-abs and IR-sct measurements IR absorbance measurements do not show any proper response with respect to the dilution series. IR-abs measured for the sample at various dilutions is shown in Figure 25. IR-abs had lots of measurement noise.

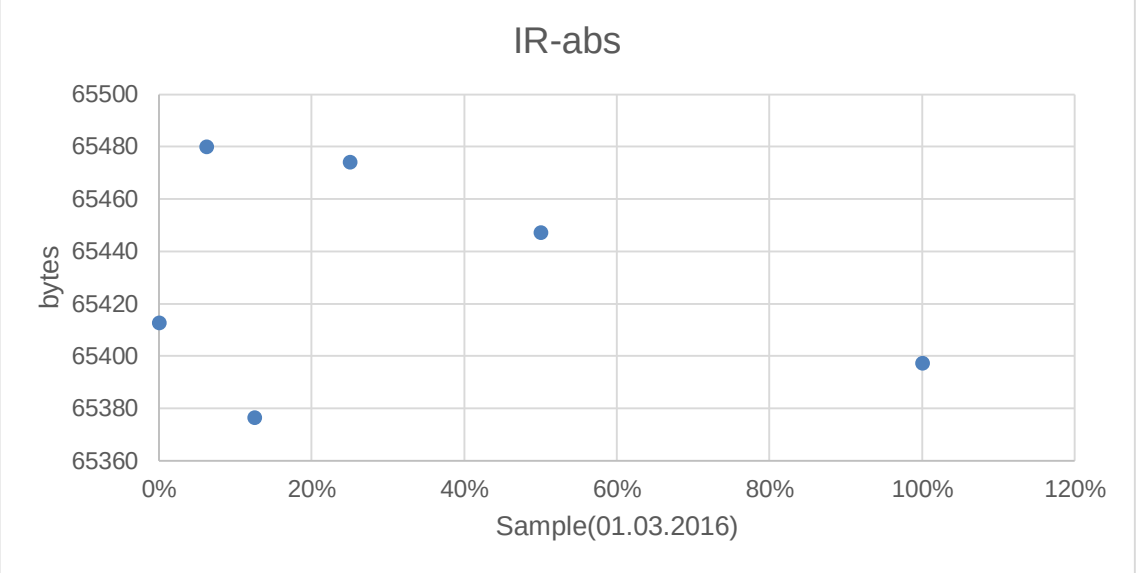



*Figure 25: IR-abs measurement of a dilution series*

The response of the conductivity measurement is similar to the IR-abs. The conductivity measured for the dilution series of the sample is shown in Figure 26. The response of the measurement suffered a lack of fit.

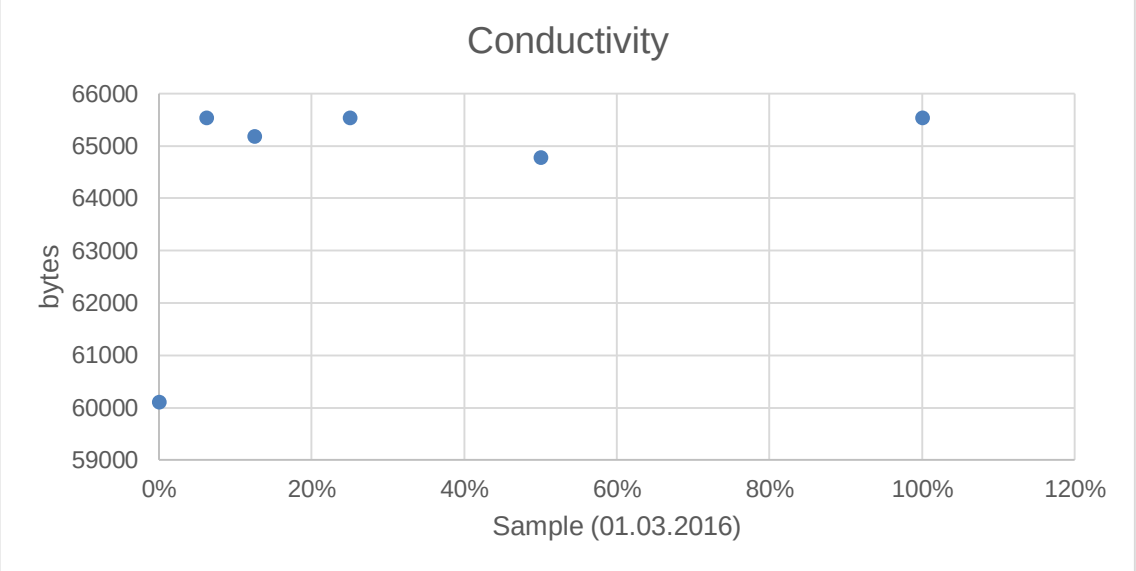



*Figure 26: Conductivity measurement of a dilution series*

Exponential or linear relationship for IR-abs or conductivity vs concentration can be observed depending upon the diluting agent. But these results show a lot of measurement noises.

## 7.3 Comparison between the laboratory and the prototype results

Depending upon the parameters either a specific or a group of samples were chosen for the comparison. Parameters with a linear or good response from the prototype as discussed in the previous chapter are further compared in this chapter. All the comparisons are based on the normalized data values.

Samples from the 5th dispatch were used to compare the UV-abs results between the lab and the prototype measurement. The measurement scale of UV-abs in the prototype and the spectrophotometer was alternating or upside down compared to each other. Hence the data from the prototype was altered into the same scale for ease in the result comparison. The comparison UV-abs measurement is shown in Figure 27.

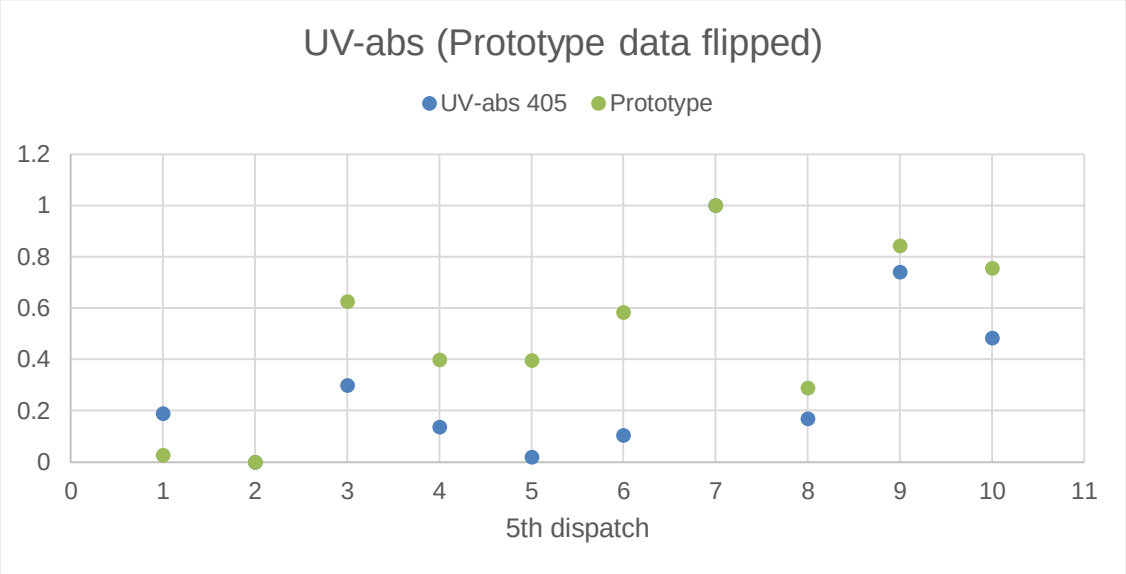



*Figure 27: Comparison between lab and prototype UV-abs measurement*

UV-abs between the prototype and the lab measurement is plotted in Figure 28. The plot is based on the samples from the fifth dispatch each with two replicates. And the correlation yielded is good. However, this is not the case in other dispatches. Due to the variation of the sample quality during the time span there are much higher deviations. Comparison of samples from all dispatches is included in Appendix 7.

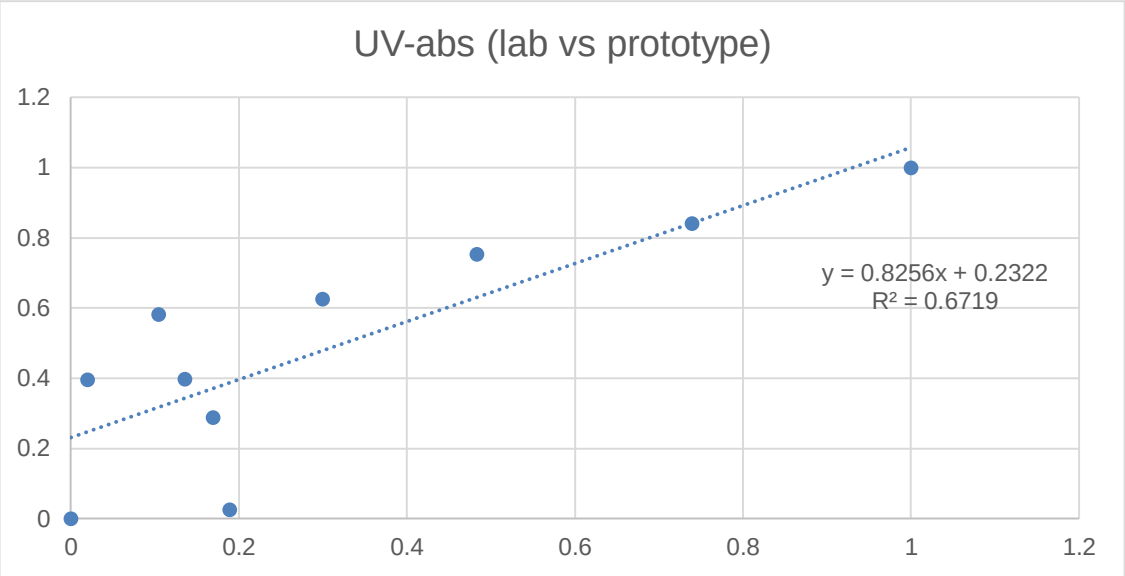



*Figure 28: Correlation between the lab and the prototype UV-abs*

For the comparison of IR-abs, turbidity and conductivity was done using the sample from the date 01.03.2016.

IR-abs from the prototype was compared with the laboratory measured TSS value. TSS was measured for only 100 % concentrated sample so for the rest of the dilution series theoretical value of TSS was used. The normalized data compared for IR-abs vs TSS measurement is shown in Figure 29.

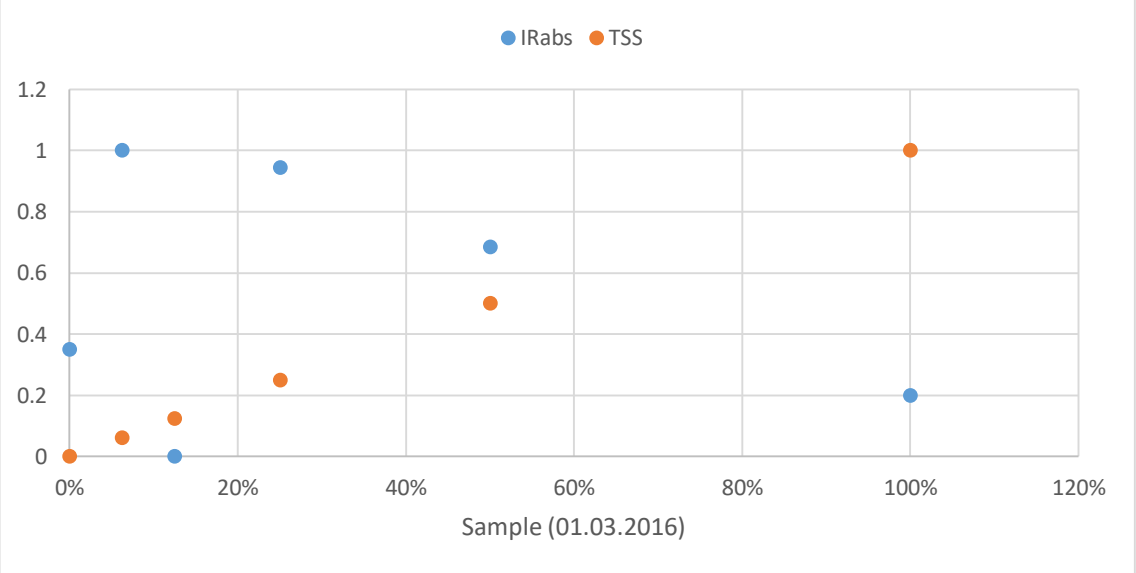



*Figure 29: Comparison between IR-abs and TSS*

IR-sct from the prototype was compared with the laboratory measured turbidity value. Unlike TSS, turbidity was measured for all dilution series. Hence the comparison was based on the actual measured values. The normalized data compared for IR-sct and turbidity measurement is shown in Figure 30.

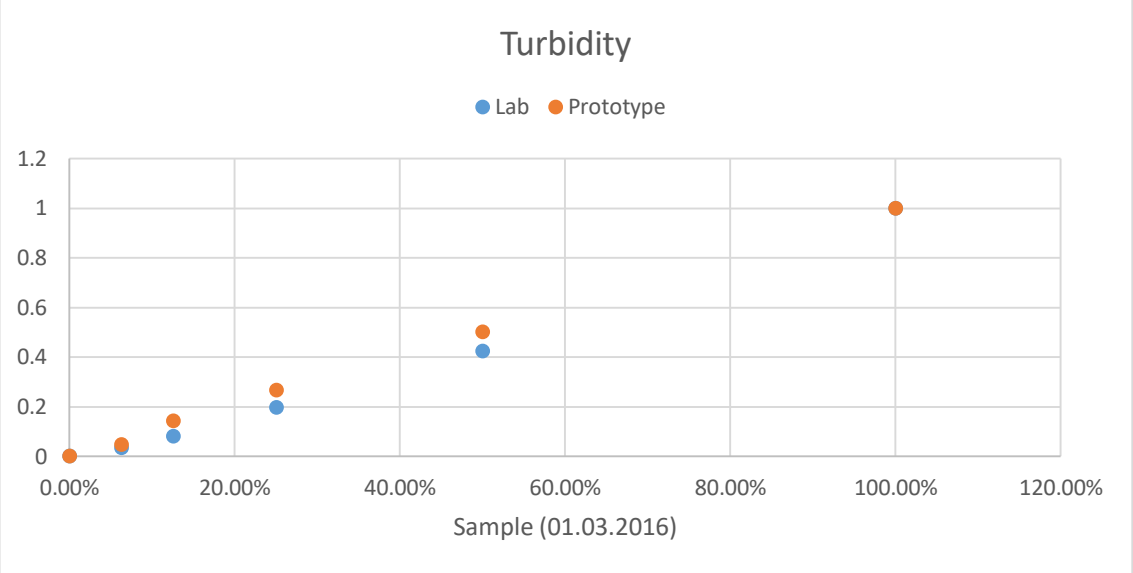



*Figure 30: Comparison of lab and prototype turbidity measurement*

Similar to the turbidity measurement, conductivity was measured for all the dilution series. Figure 31 shows the normalized comparison between lab and the prototype conductivity measurement.

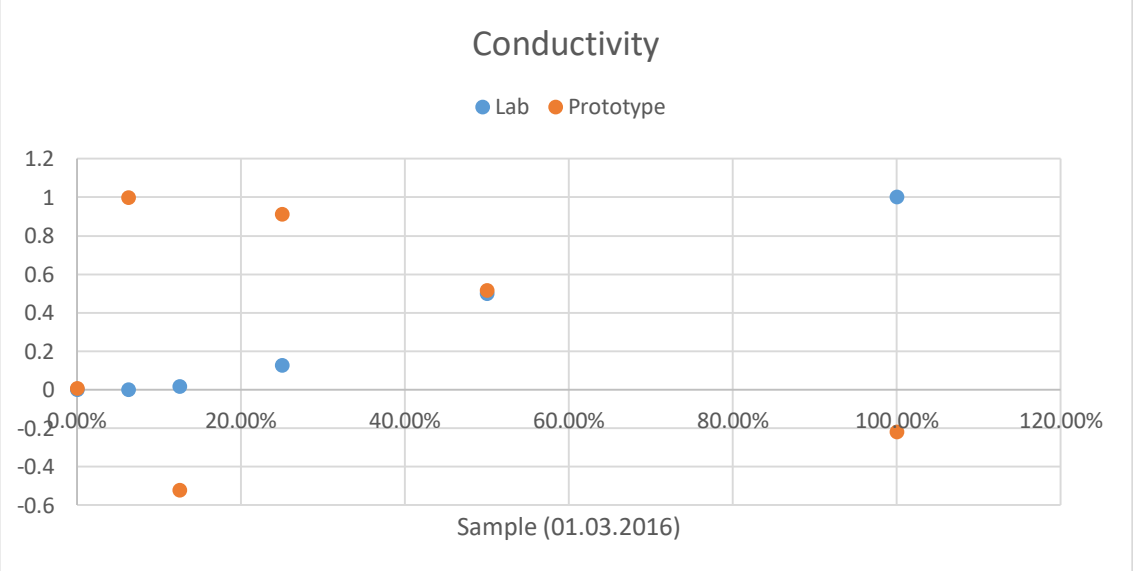



*Figure 31: Comparison of lab and prototype Conductivity measurement*

The outliers in the results indicate that IR-abs and conductivity measurements of the prototype are out of range.

## 7.4 Comparing online data from the mill with the lab measurement

In this chapter online data from the mill is compared with the laboratory measurements. The comparison was made to observe the correlation between the lab measured parameters (TSS, Turbidity, EC and COD) with the mill's online measured parameters (UV-abs, IR-abs and IR-sct). Due to a maintenance issue in the mill only 16 samples from 29.02.2016 till 29.03.2016 are compared. The measurements were overlaid with each other by matching the exact timestamps i.e. time of the online measurement coincides with the time when the sample was taken. All the data were normalized for ease in comparison. The raw data from the mill is included in Appendix 6. Figure 32 is the normalized over view of first set of the parameters expected to correlate with each other. The points are connected with a solid line for easy visual detection of correlation.

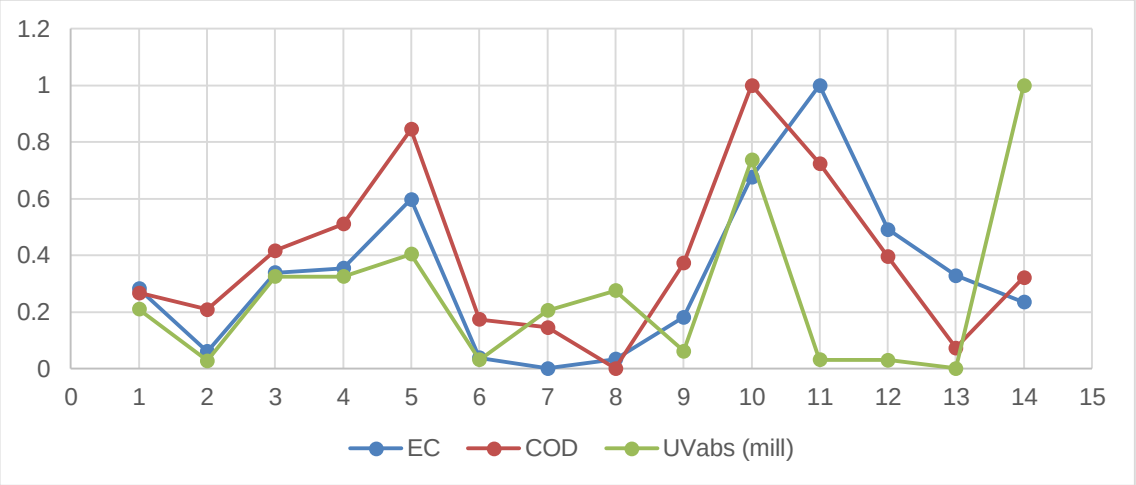



*Figure 32: Normalized comparison of laboratory EC and COD with UV-abs (mill)*

The graphs in Figure 33 and Figure 34 indicate that there is a better correlation of UV-abs with COD than with EC. However, the correlation between UV-abs and COD is very weak.

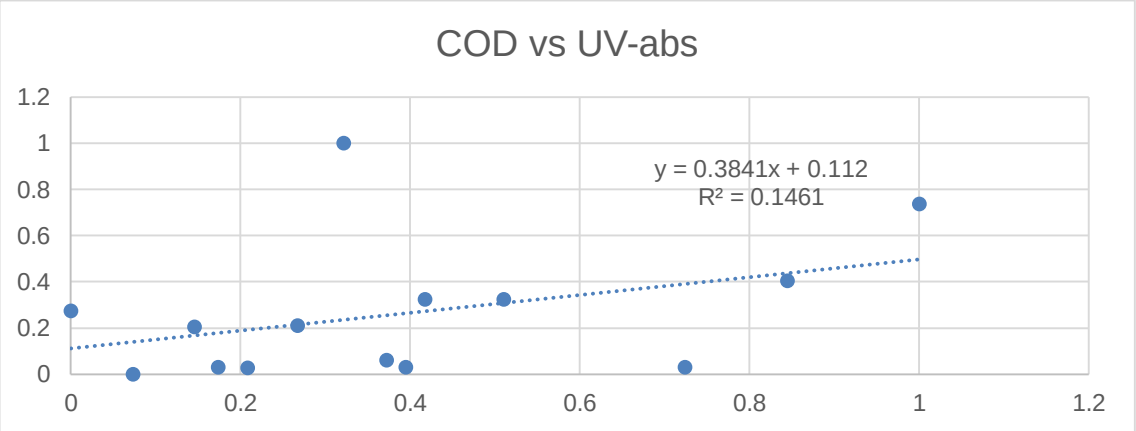



*Figure 33: Correlation of laboratory COD and UV-abs (mill)*

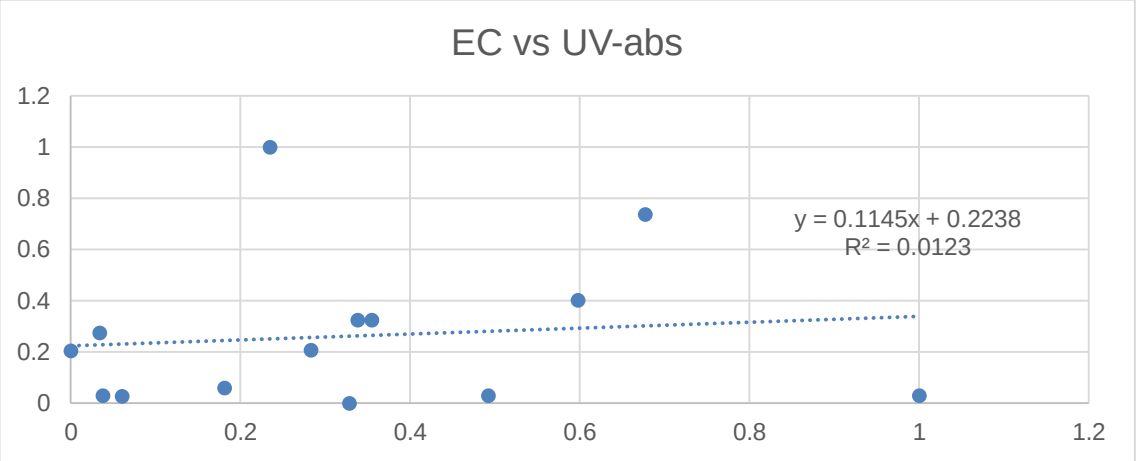



*Figure 34: Correlation of laboratory EC measurement and UV-abs (mill)*

This is a classical case where correlation can be observed visually but not statistically. This issue is observed due to the deviation in the data. Hence simple correlation analysis is not adequate in this case. Deviation is good somedays but bad on other days hence the correlation varies from day to day. Principle Component Analysis (PCA) or Partial Least Square (PLS) modeling is required to analyze the variation in details.

Figure 35 is the comparison of the second sets of the parameters, measured in the lab and the online measurement (from the mill) which are expected to have some correlation. The points are connected with a solid line for easy visual detection of correlation.

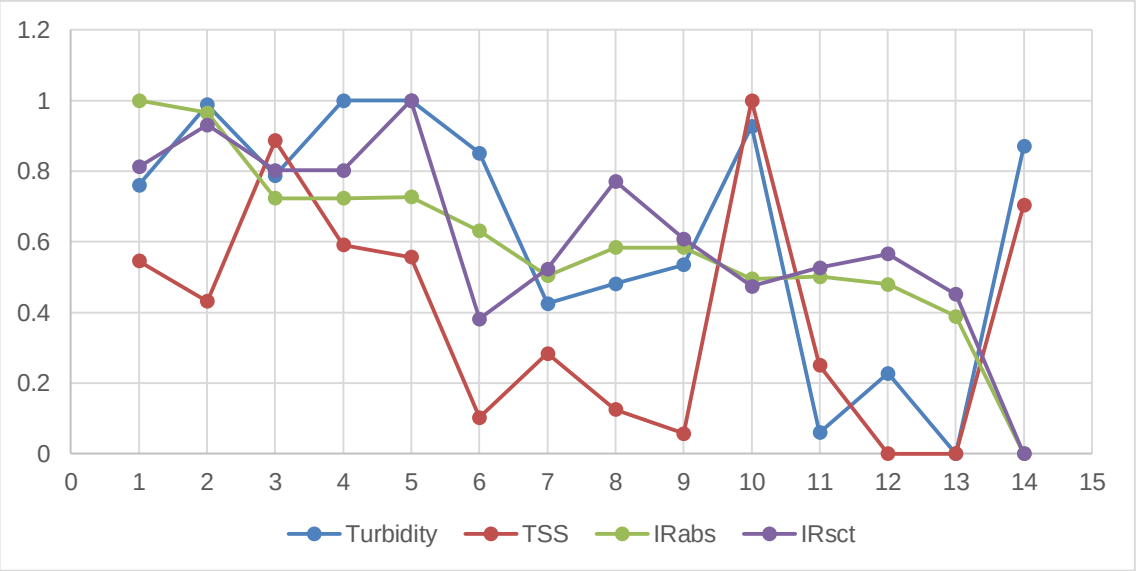



*Figure 35: Comparison of (lab) turbidity and TSS with (mill) IR-abs and IR-sct*

Unlike expected the laboratory turbidity and TSS measurement did not show any good correlation with IR-abs and IR-sct. Figure 36, Figure 37, Figure 38 and Figure 39 indicate IR-abs and IR-sct have better correlation with turbidity compared to TSS.

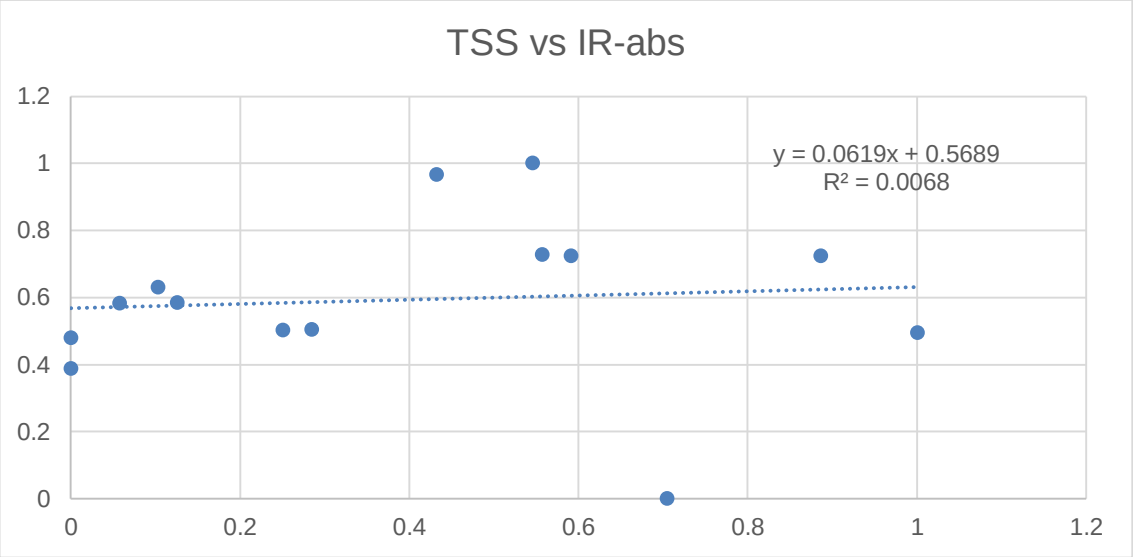



*Figure 36: Correlation between TSS(laboratory) and IR-abs(mill)*

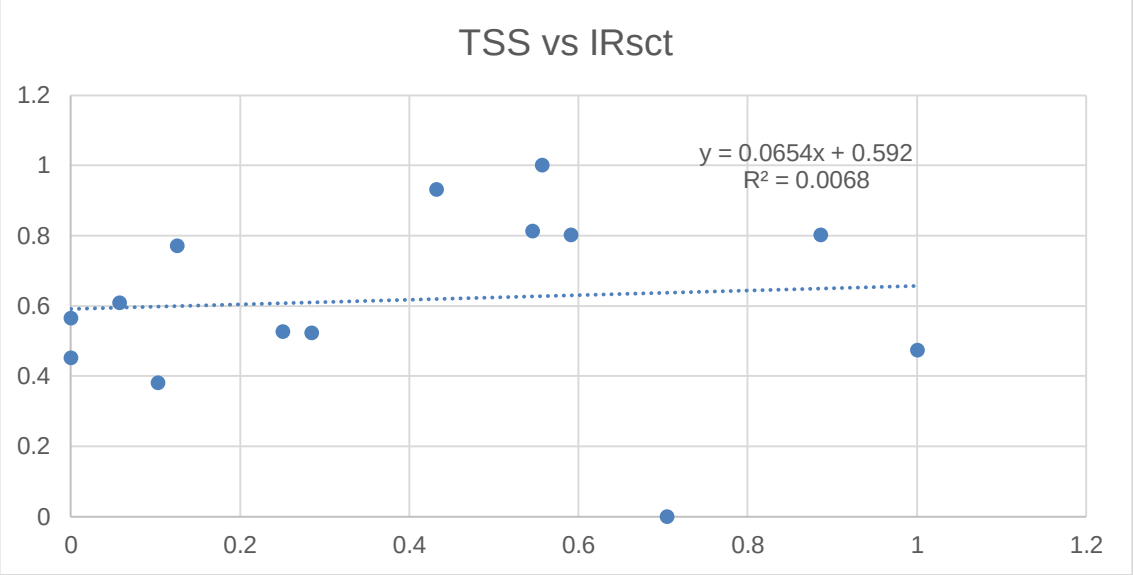



*Figure 37: Correlation between TSS (laboratory) and IR-sct(mill)*

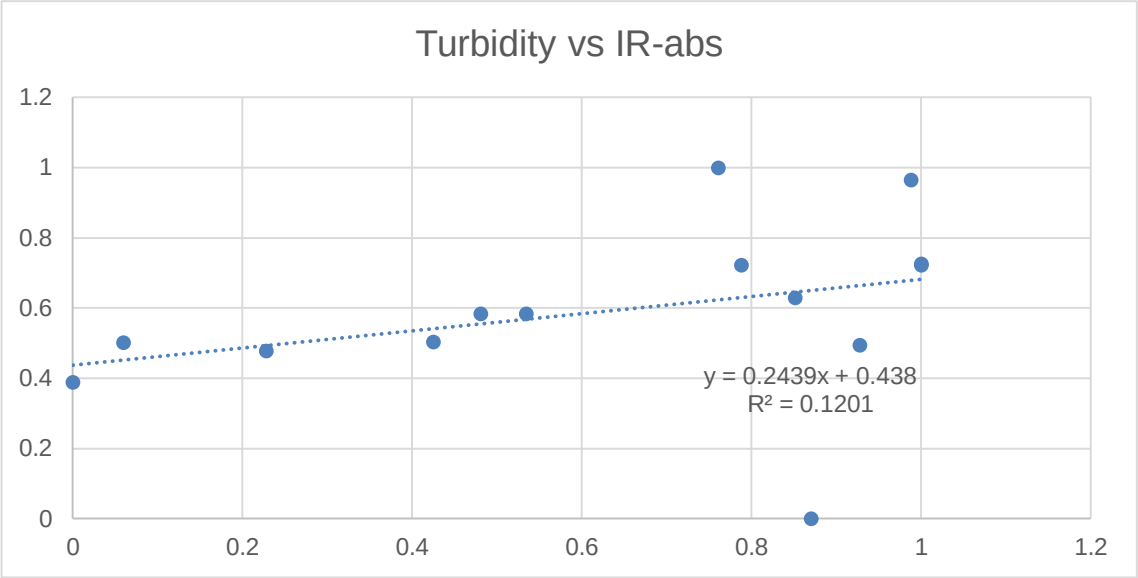



*Figure 38: Correlation between Turbidity (lab) and IR-abs (mill)*

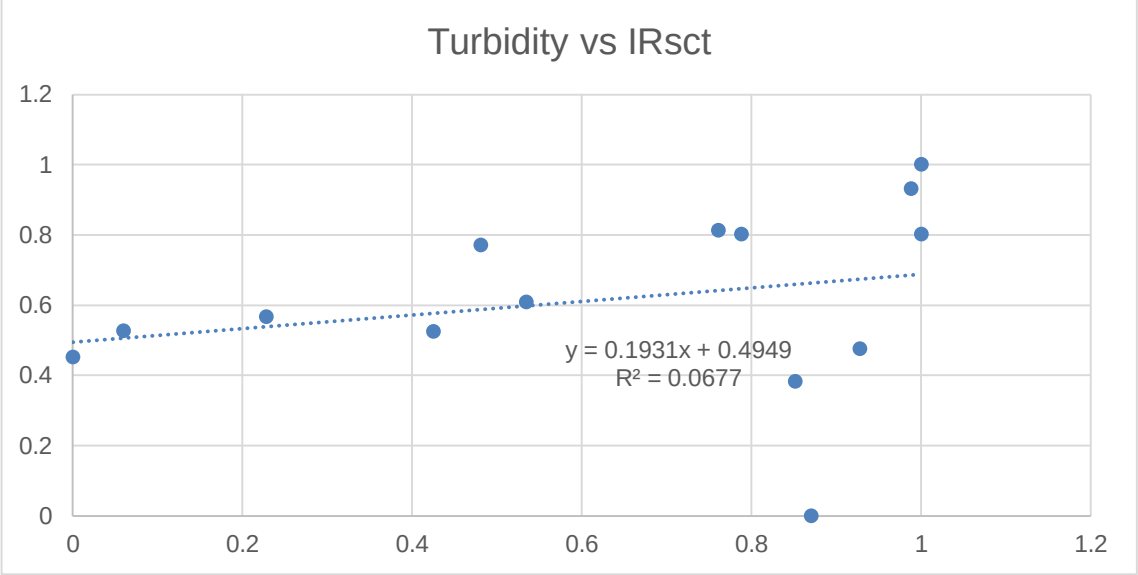



*Figure 39: Correlation between Turbidity (lab) and IR-sct (mill)*

# 8 GENERAL OBSERVATIONS AND FINDINGS

This chapter consists of interesting observations and findings during the study. These findings however require further investigations and studies to draw any significant conclusions.

## 8.1 Blue color

According to Langis Oy blue color should somehow correlate with the COD or UV-abs of the sample Figure 40 is the normalized comparison of these three parameters. The points are connected with a solid line for easy visual detection of correlation.

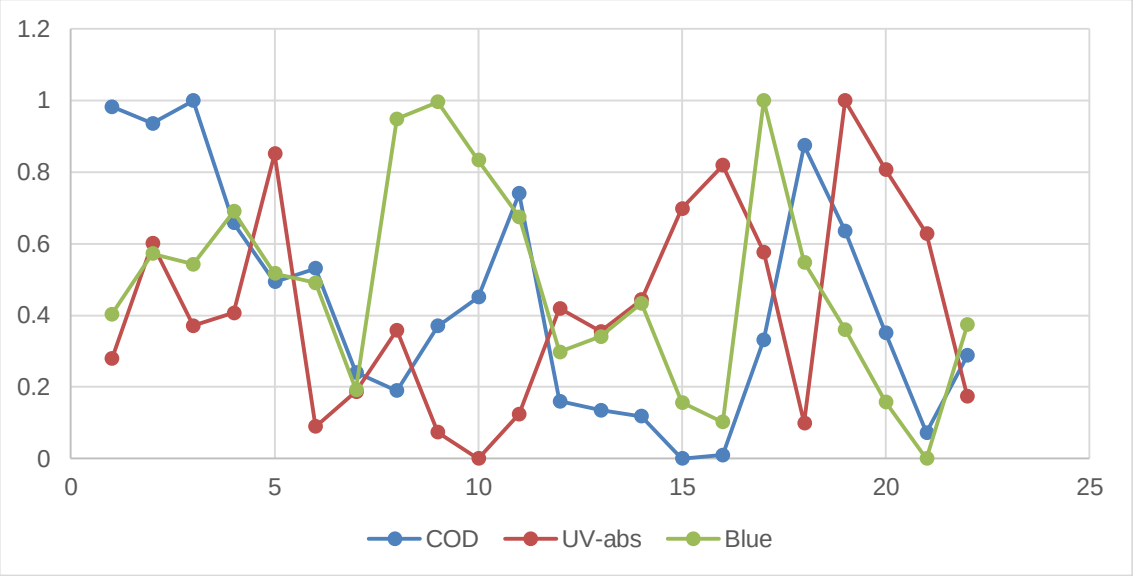



*Figure 40: Comparison between COD, UV-abs and Blue*

When the parameters were further plotted against each other, a very weak correlation is discovered. The correlation is shown in Figure 41.

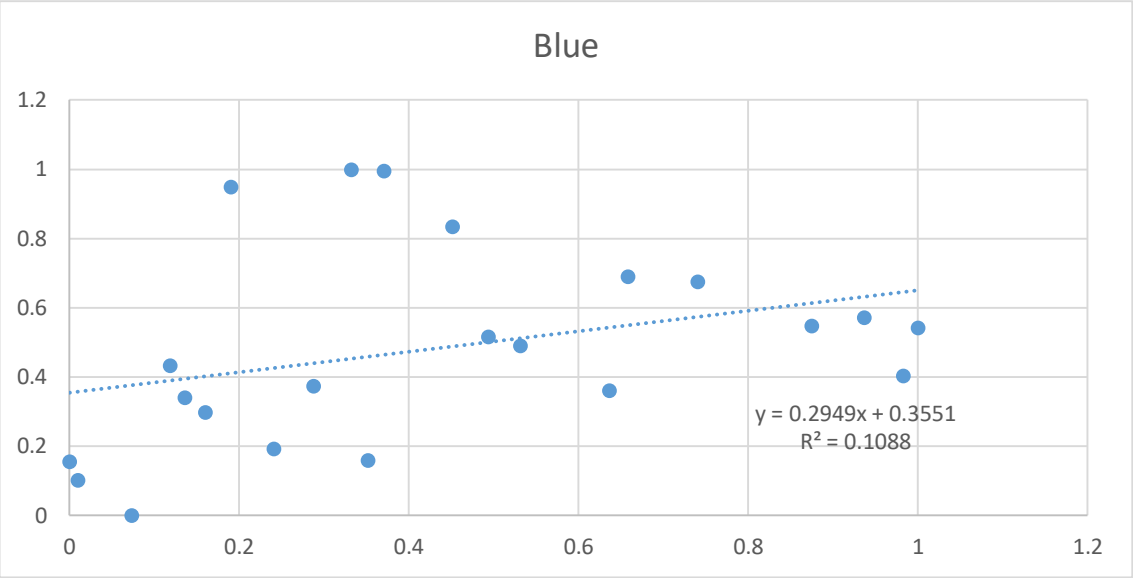



*Figure 41: Correlation of Blue color with COD*

## 8.2 Calibration of the prototype

This chapter consists of a study of the samples from the fifth dispatch. All the samples with the respective dilution series are plotted in the same graph to see the precision of the prototype. The data were analyzed by comparing the turbidity with IR-sct. These parameters had nice correlation with each other as mentioned in the previous Chapter 7.3. Moreover, correlation between COD and UV-abs was also analyzed. UV-abs as discussed in the Chapter 7.2 had nice response with respect to the dilution or concentration of the sample.

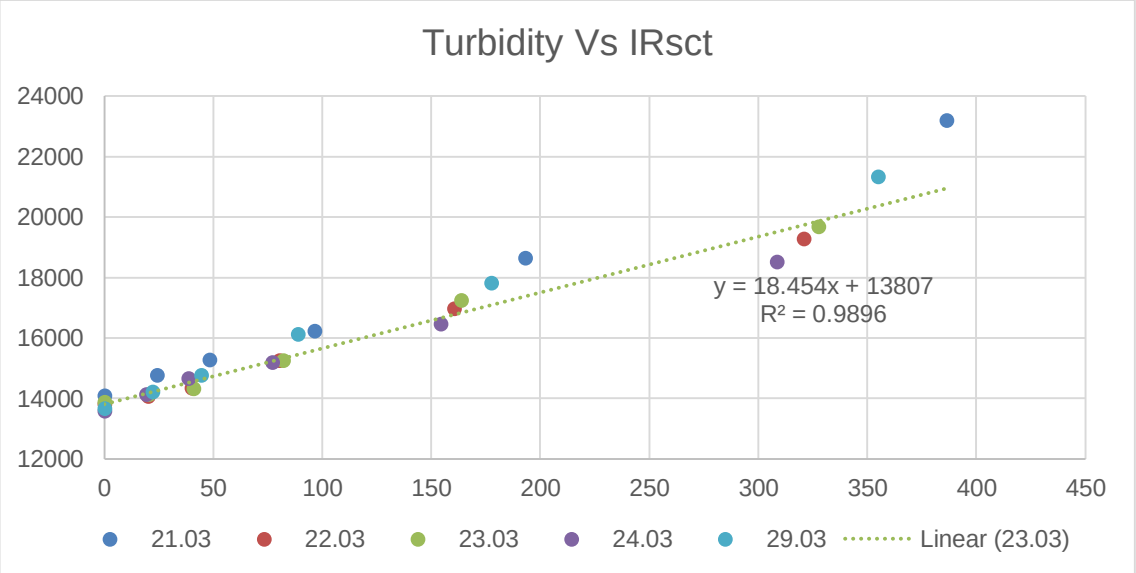



*Figure 42: Turbidity vs IR-sct of the samples with dilution series*

Figure 42 establishes nice relationship as a degree of dilution and the samples taken during different dates with varying turbidity. There is some kind of effect that causes the diluted samples to deviate from the general relation of each concentration size. This could be because of the particle size or turbidity or color or the optical phenomenon. But the actual reason behind this effect is not known yet. Turbidity range of 300 to 400 NTU could be predicted using prototype for 100% concentration based on the samples taken into consideration.

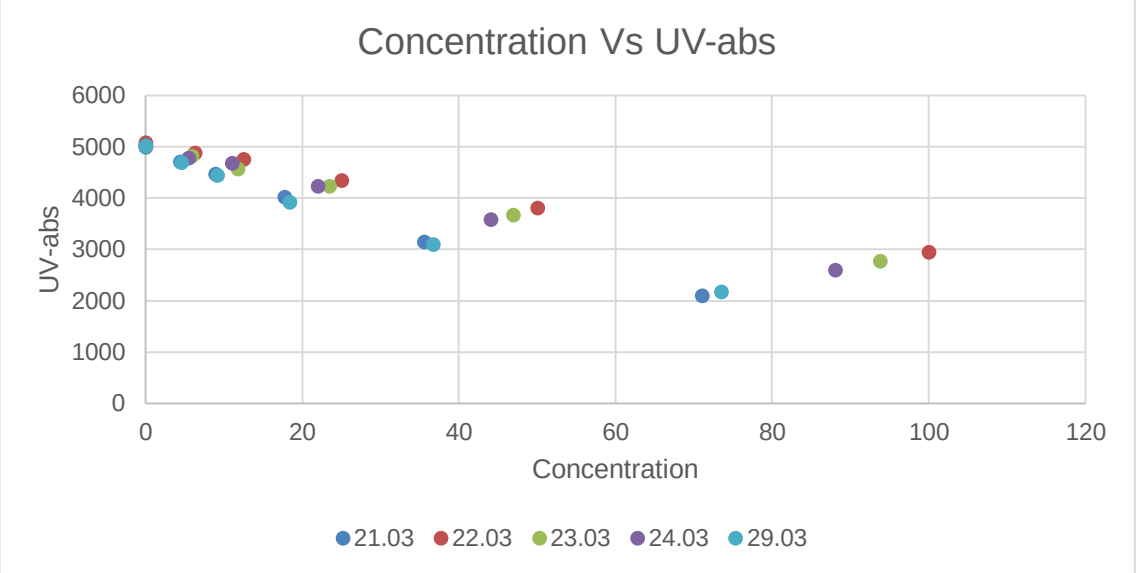



*Figure 43: Concentration vs UV-abs of the samples*

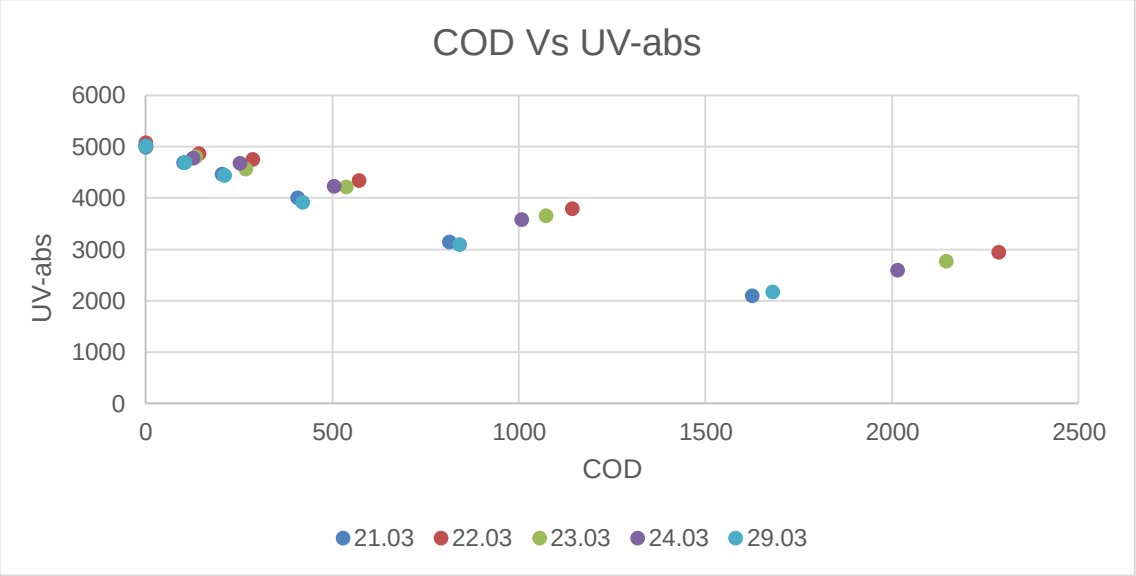



*Figure 44: COD vs UV-abs of the samples with dilution series*

Figure 43 and Figure 44 also establish good relationship as a degree of dilution with respect to the UV-abs measurement and the samples taken during different dates with varying COD levels. There is also similar kind of effect as mentioned earlier hence the general relation is not established in this case. This effect could be the result of similar but various factors like the particle size, varying COD levels, color and or the optical phenomenon. The actual reason behind this phenomenon is yet to be discovered. COD range between 1500 to 2500 mg/l could be predicted using the prototype for 100% concentration based on the samples taken into consideration.

This data analysis unfolds an important practical issue relating to the calibration of the sensor. Every dilution series has a different linear function compared to a general linear trend representing each concentration. The linear function of 100% concentrated samples deviate from the linear dilution trend. So, the prototype should be calibrated using the samples from different dates but not the dilution series along with laboratory follow up. The calibration might follow some other relationship with IR-abs, turbidity, EC and COD.

## 8.3 Milk sample analysis

Milk was used during the study in order to check the goodness of the IR-sct measurement. Several concentrations of milk samples were prepared (Table 3). The prototype was responding to every concentration of the milk samples even the laboratory turbidimeter was unable to precisely measure any of the samples prepared. But the result analysis revealed the IR-sct measurement was out of order. Surprisingly IR-abs was working without showing any signs of out scaling. IR-abs measured for the milk sample is shown in Figure 45.

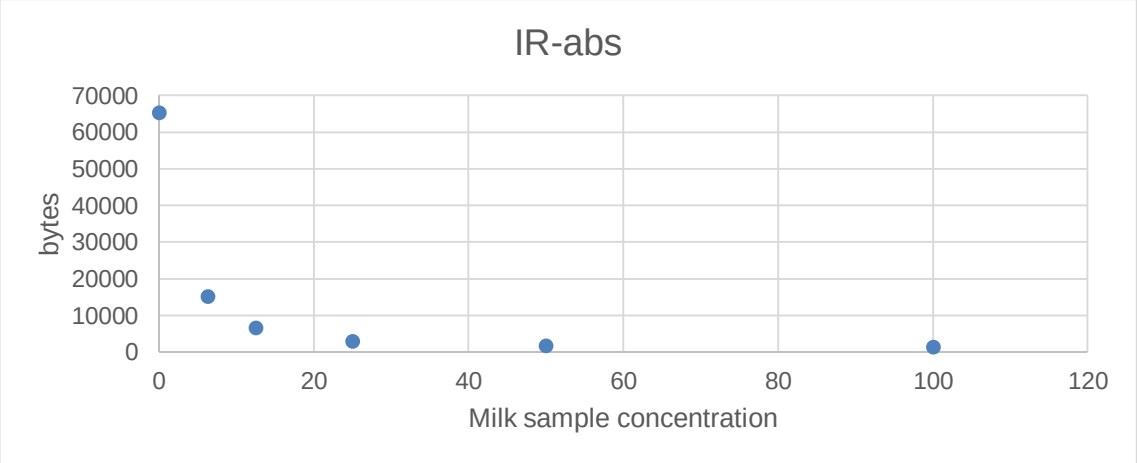



*Figure 45: IR-abs observed against milk sample*

# 9 GENERAL DISCUSSION

50 % diluted samples using ion exchanged water were used in the experiments to determine the TSS. This decision was made due to the persistent clogging of the filter paper while using 100 % samples. Similarly, the filter paper was weighed directly without drying in the oven before the filtration. According to the experience of an innovation project team, there was no any difference in the mass of the filter paper with and without drying before the filtration (Jaffry, et al., 2016).

COD analysis was performed for the filtered sample rather than for the original sample. Langis Oy was interested in the COD level due to the presence of the dissolved solids (TDS) rather than the TSS.

Interference of the ambient light during the experimentation was neglected. A test performed in the presence and absence of the ambient light indicated that measurement range for all parameters were higher when the ambient light was cut off. Unlike other parameters color measurement could not be analyzed and estimated based on the dilution pattern. The compact design several LEDS in the same prototype might have some interference in itself.

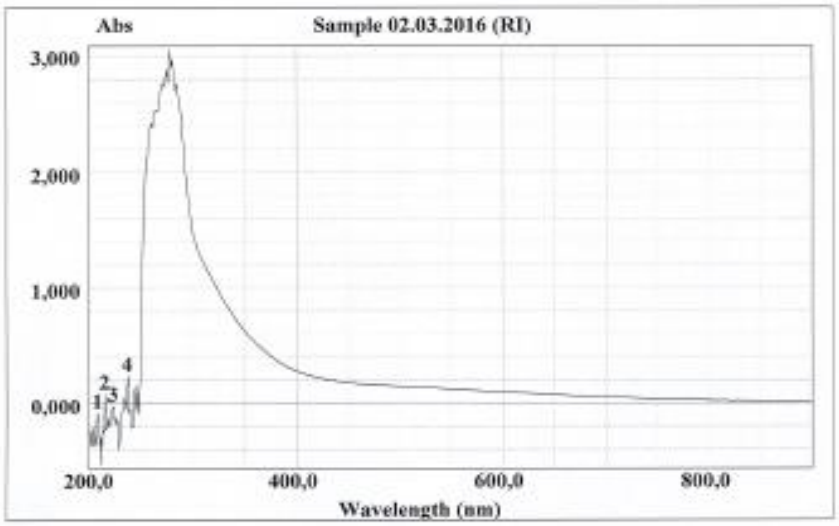
There was also certain complexity with EC measurement. The prototype had very narrow range of conductivity measurement. Hence, reconfiguring the EC was suggested.

The prototype uses UV radiation of 405 nm for the measurement of UV-abs. However, the spectrophotometric analysis performed in the lab indicates the maximum absorbance for the samples is in between the wavelength of 200 to 400 nm (~300 nm) but not at 405 nm. Spectrophotometric analysis of a sample is shown in Figure 46. The measurement scale of UV-abs in the prototype was opposite compared to the spectrophotometer. Measurement noises were visible in the UV measurement. This could be due to the interference of SS in the sample. The LED for the measurement of UV-abs emits the radiation of wavelength 405 nm. Visible spectrum starts form 400 nm hence the light emitted is in fact a blue light but not a UV radiation.

16:59:53 27.4.2016

# Biochrom Ltd

| | |
|---|---|
| Title | Sample 02.03.2016 (RI) |
| Operator | Bijay Karki |
| Filename | Scan-1 (27-04-16 16-59) |
| Date | 27.4.2016 |
| Time | 16:59:31 |
| Comments | |
| Start Wavelength | 200,0 nm |
| End Wavelength | 900,0 nm |
| Scan Step | 1,0 nm |
| Scan Speed | 6000 nm/min |
| Temperature | Off |




| Type | Sensitivity |
|---|---|
| Peak | 16 |

| | |
|---|---|
| Convolution width | Medium |
| Interpolate peak heights | Off |
| Source data | Original data |

| No. | Peak Type | Position | Height |
|---|---|---|---|
| 1 | Peak | 208,8 | -0,086 |
| 2 | Peak | 216,0 | 0,079 |
| 3 | Peak | 223,6 | -0,029 |
| 4 | Peak | 237,7 | 0,235 |
| 5 | Peak | 279,1 | 3,051 |

*Figure 46: Laboratory spectrophotometric analysis*

# 10 BUDGET

The expenses incurred in this thesis project are presented in this chapter. Only consumable items used are considered as an expense made. Hence, it does not include any equipment borrowed either from Metropolia UAS or Langis Oy.

*Table 5: Cost evaluation*

| **Description** | **Quantity** | **Amount** |
|---|---|---|
| Filter paper (0.45 µm) | 3 packs | 30 € |
| LCK 514 | 2 packs | 130.2 € |
| Milk (sample) | 1 liter | 1.6 € |
| | Total | 161.8 € |

Cost of the ion-exchanged water used and the delivery cost of waste water samples to Metropolia by the mill are not included. Hence, the total cost for this thesis sums to 161.8 € in total.

# 11 CONCLUSION

The aims of this thesis were

- Characterization of waste water samples from the pulp and paper mill using the new prototype manufactured by Langis.
- Comparison of the results with the online data and lab measurements for reliability.
- Monitoring the performance and checking for any flaws in the prototype during the study period.

Similarly, a sub-question of this study was how does the COD correlate with UV-absorbance and IR-absorbance for the given pulp and paper sample?

The results obtained from the thesis project showed, the waste water samples could not be characterized solely using the prototype. Laboratory experiments were performed in order to complete, compare and verify the prototype measurements. All the lab equipment was calibrated as required during this thesis. The results produced from the lab were considered accurate but experimental and systematic errors were neglected. Online measurement from the mill was also compared with the laboratory measurement.

The main findings of this thesis is the correlation between the parameters measured from the samples. The laboratory measurement of the samples confirmed COD and EC had a very good correlation (Figure 21). Similarly, TSS and turbidity also had nice correlation with each other (Figure 22). Response of the prototype was assessed using different samples against varying concentrations. UV-abs and IR-sct measurements had very good response with respect to the dilution series (Figure 15 and Figure 16). In fact, IR-sct correlates very well with the turbidity measurement. UV-abs measurement also had measurement noises, but the calibration curve using the average value produces a linear fit. However, the correlation between UV-abs and COD was very weak. IR-abs and conductivity measurements on the other hand were out of range, hence did not yield proper responses as expected (Figure 17 and Figure 18). IR-abs had too much measurement noise. Similarly, the range of EC measurement was very narrow.

Online control system of the mill should be based on the online measurement of EC, SS and turbidity. These parameters show good correlation among each other and help in estimating the COD level.

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# Appendices

## Appendix 1. Operational Instructions of the prototype

This is a basic and stepwise description on how to take measurements using the prototype.

1. Raspberry Pi (Raspi) needs a monitor with HDMI and USB input devices (keyboard and mouse).

It is suggested to make all the required connections before connecting to the power source.

2. Raspi operates in five volts (5 V) hence the power should be supplied using an appropriate adapter. The prototype is IP68 rated and can be immersed to water.

After the power connection Raspi starts to boot. This is visible in the screen. Raspi opens without password. After the booting is completed desktop screen appears.

3. When the desktop screen is ready open the terminal window (black icon on the top).

4. Type a command "*sudo idle*" in the terminal window. This command opens the Python editor.

5. In the Python editor click on “File” menu then from the dropdown menu choose "Recent files" and open “*DATALOG3_21*.py”.

This opens the codes programmed to run the prototype. (The codes were saved under the file name *DATALOG3_21*.py in this study)

6. When the file opens click on the “Run” menu to run the codes.

7. There will be a visualization screen and a small UI (User Interface).

Visualization screen plots graph from the online measurements. UI gives control to the user to start, pause and stop measurement.

8. Data file is created and stored in the Desktop and is labelled by timestamp.

Whenever the code is started a new data file is generated. The data in the file are stored in CSV (comma separated variables) format. However, without proper internet connection the timestamp might not correspond to the real time.

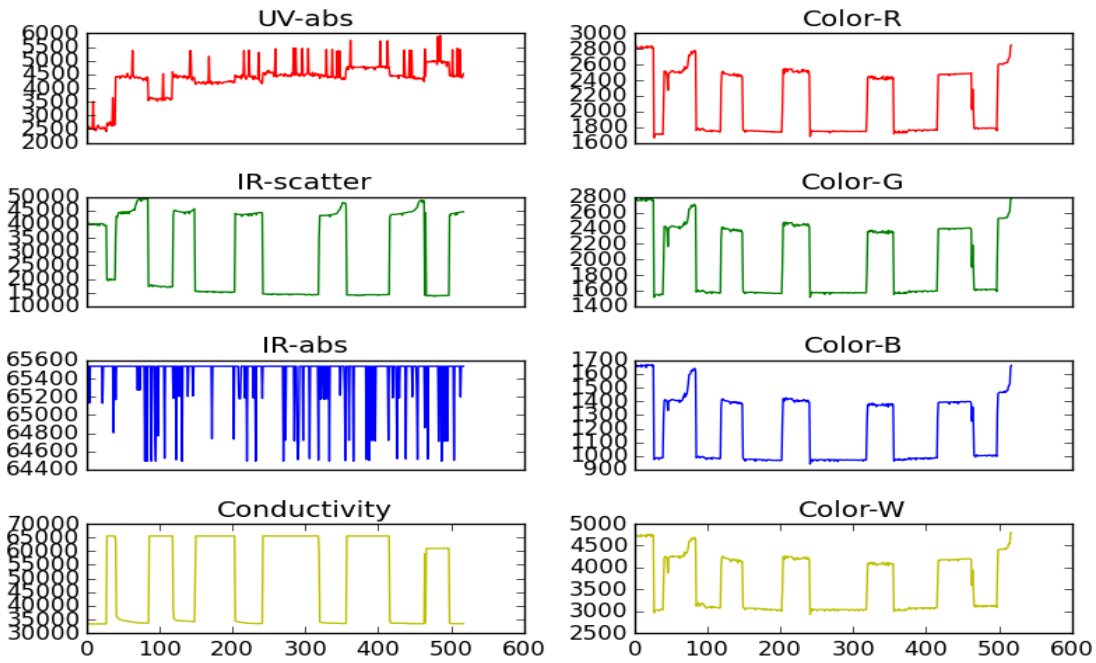
9. The prototype measures UV absorbance, IR scattered, IR absorbance, Conductivity and RGBW (color) spectrum.

10. The data file contains only 9 columns of data; the first column is timestamp while the others are the parameters mentioned in the step 9. The indexes of data columns (UV, IR, Cond, RGBW) are also indicated in the code.

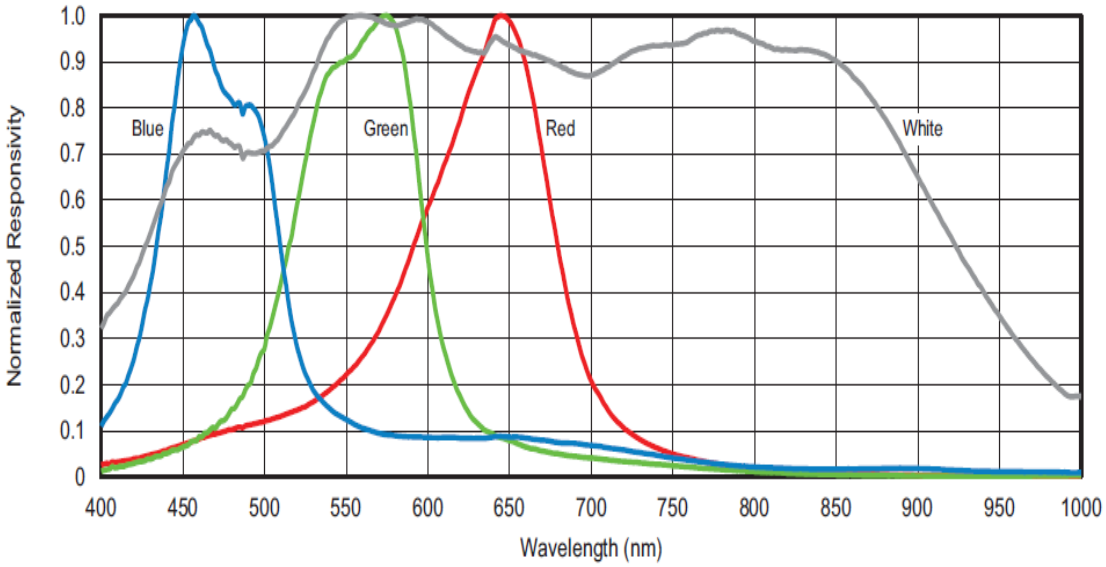
The prototype also measures other parameters since it does a "sweep" with different LED intensities and temperatures of sensor LEDs are also measured. However, these measurements were suppressed in the data file.

11. When all the required measurements are taken, transfer the data file to a USB stick and close the Raspi by typing a command "*sudo halt -p*" in the terminal window.

## Appendix 2. An example of online graphical plot for a dilution series




## Appendix 3. Response of the color sensor with respect to the wavelength



## Appendix 4. Results from laboratory measurements

Following table consists of results from laboratory analysis of the samples. Two replicated samples were used to determine TSS and COD for each sample. While measuring EC and turbidity accuracy of the measuring devices was accessed.

| Sample | | EC (µS/cm) | | Turbidity (NTU) | | TSS (mg/l) | | COD (mg/l) | |
|---|---|---|---|---|---|---|---|---|---|
| *Date* | *Time* | *Average* | *Accuracy* | *Average* | *Accuracy* | *Average* | *SD* | *Average* | *SD* |
| 22.02.2016 | 7:00 | 3040.0 | N/A | 435.0 | 0.5 | 364.0 | N/A | 2716.3 | 16 |
| 23.02.2016 | 7:21 | 3040.0 | N/A | 238.3 | 3.8 | 288.0 | 12.0 | 2659.0 | 16 |
| 23.02.2016 | 7:24 | 3180.0 | N/A | 283.7 | 2.3 | 312.0 | 12.0 | 2738.3 | 18 |
| 24.02.2016 | 7:30 | 3230.0 | 20.0 | 389.0 | N/A | 254.0 | 22.0 | 2313.0 | 201 |
| 25.02.2016 | 7:42 | 3010.0 | N/A | 224.0 | 0.0 | 228.0 | 12.0 | 2108.7 | 17 |
| 26.02.2016 | 7:41 | 2720.0 | 0.0 | 519.0 | 1.7 | 310.0 | 2.0 | 2155.3 | 18 |
| 29.02.2016 | 7:40 | 2196.7 | 4.7 | 339.7 | 3.7 | 326.0 | 12.0 | 1794.7 | 201 |
| 01.03.2016 | 7:30 | 1825.0 | 17.1 | 403.3 | 2.1 | 306.0 | 6.0 | 1731.7 | 8 |
| 02.03.2016 | 7:45 | 2290.0 | 17.0 | 347.3 | 0.5 | 386.0 | 26.0 | 1956.0 | 44 |
| 03.03.2016 | 7:45 | 2316.7 | 30.9 | 406.7 | 4.2 | 334.0 | 6.0 | 2056.0 | 20 |
| 04.03.2016 | 7:03 | 2723.3 | 17.0 | 406.7 | 0.5 | 328.0 | 4.0 | 2415.7 | 27 |
| 15.03.2016 | 7:45 | 1786.7 | 6.5 | 365.0 | 2.6 | 248.0 | 4.0 | 1694.3 | 22 |
| 16.03.2016 | 7:45 | 1724.3 | 12.1 | 245.7 | 1.7 | 280.0 | 6.0 | 1664.0 | 11 |
| 16.03.2016 | 7:45 | 1732.7 | 18.5 | 219.7 | 1.2 | 268.0 | 6.0 | 1642.7 | 11 |
| 17.03.2016 | 7:38 | 1784.3 | 3.7 | 214.7 | 1.7 | 272.0 | 10.0 | 1495.7 | 12 |
| 17.03.2016 | 7:38 | 1780.0 | 4.2 | 261.3 | 2.1 | 252.0 | 10.0 | 1508.0 | 12 |
| 18.03.2016 | 7:37 | 2026.7 | 12.5 | 276.3 | 0.9 | 240.0 | 32.0 | 1907.7 | 9 |
| 21.03.2016 | 7:35 | 2856.7 | 34.9 | 386.3 | 0.9 | 406.0 | 26.0 | 2582.3 | 130 |
| 22.03.2016 | 7:35 | 3396.7 | 46.7 | 143.3 | 0.5 | 274.0 | 2.0 | 2285.7 | 38 |
| 23.03.2016 | 7:37 | 2546.7 | 34.9 | 190.3 | 0.5 | 230.0 | 14.0 | 1932.0 | 40 |
| 24.03.2016 | 6:23 | 2273.3 | 23.6 | 126.7 | 0.5 | 230.0 | 2.0 | 1586.0 | 10 |
| 29.03.2016 | 7:45 | 2116.7 | 30.8 | 370.3 | 1.7 | 354.0 | 14.0 | 1853.0 | 43 |

## Appendix 5. Results from prototype measurements

Following table is the result obtained on measuring the samples using the prototype.

| Dispatch | Sample | UV-abs (bytes) | | IRscat (bytes) | | IR-abs (bytes) | | Conductivity (bytes) | |
|---|---|---|---|---|---|---|---|---|---|
| | | Average | Accuracy | Average | Accuracy | Average | Accuracy | Average | Accuracy |
| 2nd | 22.02.2016 | 2265.353 | 418.060 | 21723.882 | 205.234 | 65352.294 | 394.704 | 65535.000 | 0.000 |
| | 23.02.2016 | 2570.474 | 318.521 | 20614.842 | 232.123 | 65402.316 | 308.674 | 63844.105 | 0.000 |
| | 23.02.2016 | 2353.065 | 260.723 | 21303.484 | 158.432 | 65420.903 | 211.301 | 64497.774 | 0.000 |
| | 24.02.2016 | 2387.053 | 239.565 | 21950.632 | 227.400 | 65257.158 | 559.183 | 63844.316 | 0.000 |
| | 25.02.2016 | 2807.234 | 406.908 | 20897.714 | 469.583 | 65385.130 | 350.289 | 65528.247 | 0.000 |
| | 26.02.2016 | 2086.145 | 326.916 | 23611.000 | 271.756 | 65398.258 | 320.291 | 65535.000 | 0.000 |
| 3rd | 29.02.2016 | 2178.552 | 229.910 | 21947.500 | 275.462 | 65320.293 | 360.213 | 64981.000 | 0.000 |
| | 01.03.2016 | 2340.813 | 320.139 | 23316.625 | 555.806 | 65397.094 | 293.145 | 65535.000 | 0.000 |
| | 02.03.2016 | 2070.949 | 186.927 | 23684.929 | 342.527 | 65221.367 | 601.985 | 65452.286 | 264.949 |
| | 03.03.2016 | 2001.632 | 231.705 | 23574.684 | 139.794 | 65387.211 | 173.032 | 63986.474 | 0.000 |
| | 04.03.2016 | 2119.052 | 184.706 | 23612.052 | 330.612 | 65183.138 | 646.350 | 64981.017 | 0.000 |
| 4th | 15.03.2016 | 2398.814 | 190.417 | 21773.627 | 222.480 | 65480.576 | 198.968 | 65535.000 | 0.000 |
| | 16.03.2016 | 2337.694 | 375.356 | 23410.111 | 188.447 | 65487.361 | 201.126 | 65535.000 | 0.000 |
| | 16.03.2016 | 2421.352 | 275.975 | 22927.571 | 287.866 | 65426.637 | 285.019 | 65535.000 | 0.000 |
| | 17.03.2016 | 2662.775 | 283.352 | 20854.025 | 186.703 | 65335.300 | 378.299 | 65535.000 | 0.000 |
| | 17.03.2016 | 2776.750 | 209.734 | 19535.063 | 169.044 | 65372.583 | 344.391 | 65535.000 | 0.000 |
| | 18.03.2016 | 2547.781 | 299.690 | 23793.875 | 350.836 | 65353.906 | 381.631 | 65535.000 | 0.000 |
| 5th | 21.03.2016 | 2095.618 | 556.199 | 23204.059 | 194.469 | 61964.735 | 1127.982 | 64590.294 | 0.000 |
| | 22.03.2016 | 2948.000 | 220.465 | 19275.840 | 731.466 | 65175.360 | 955.486 | 65535.000 | 0.000 |
| | 23.03.2016 | 2765.417 | 269.905 | 19686.250 | 166.894 | 65474.250 | 201.485 | 65535.000 | 0.000 |
| | 24.03.2016 | 2596.708 | 211.057 | 18529.792 | 134.234 | 65363.875 | 320.034 | 64195.292 | 0.000 |
| | 29.03.2016 | 2165.939 | 435.986 | 21328.212 | 181.607 | 62817.515 | 843.769 | 65535.000 | 0.000 |

| Dispatch | Sample | Red (bytes) | | Green (bytes) | | Blue (bytes) | | White (bytes) | |
|---|---|---|---|---|---|---|---|---|---|
| | | Average | Accuracy | Average | Accuracy | Average | Accuracy | Average | Accuracy |
| 2nd | 22.02.2016 | 1675.412 | 75.280 | 1551.647 | 95.739 | 1017.647 | 69.540 | 3047.471 | 128.021 |
| | 23.02.2016 | 1661.105 | 54.292 | 1565.579 | 64.042 | 1040.526 | 46.735 | 2994.947 | 90.084 |
| | 23.02.2016 | 1673.161 | 43.240 | 1564.484 | 52.912 | 1036.548 | 38.236 | 3028.935 | 72.156 |
| | 24.02.2016 | 1727.158 | 47.209 | 1602.053 | 51.996 | 1056.526 | 35.865 | 3167.474 | 83.172 |
| | 25.02.2016 | 1724.805 | 44.038 | 1593.026 | 47.888 | 1033.052 | 33.979 | 3148.390 | 79.972 |
| | 26.02.2016 | 1756.403 | 17.918 | 1597.710 | 13.069 | 1029.565 | 5.830 | 3231.548 | 40.894 |
| 3rd | 29.02.2016 | 1620.431 | 5.468 | 1502.707 | 6.139 | 988.948 | 4.468 | 2905.759 | 11.474 |
| | 01.03.2016 | 1959.719 | 53.603 | 1749.063 | 58.123 | 1091.688 | 48.310 | 3483.125 | 118.584 |
| | 02.03.2016 | 1791.204 | 27.799 | 1662.010 | 32.609 | 1098.133 | 23.238 | 3277.133 | 47.459 |
| | 03.03.2016 | 1776.053 | 60.777 | 1643.526 | 74.976 | 1076.053 | 54.463 | 3253.579 | 105.124 |
| | 04.03.2016 | 1771.724 | 37.219 | 1623.172 | 43.983 | 1054.517 | 32.758 | 3250.879 | 61.162 |
| 4th | 15.03.2016 | 1696.203 | 9.074 | 1547.695 | 11.191 | 1003.339 | 6.617 | 3125.508 | 18.861 |
| | 16.03.2016 | 1710.528 | 12.835 | 1554.722 | 10.112 | 1009.111 | 6.022 | 3208.194 | 24.719 |
| | 16.03.2016 | 1729.890 | 49.028 | 1577.637 | 58.092 | 1021.725 | 43.023 | 3253.407 | 84.072 |
| | 17.03.2016 | 1642.525 | 9.992 | 1508.975 | 8.601 | 984.100 | 6.090 | 3040.675 | 22.536 |
| | 17.03.2016 | 1621.479 | 5.212 | 1494.813 | 6.040 | 976.771 | 4.736 | 2972.396 | 15.008 |
| | 18.03.2016 | 1942.438 | 24.784 | 1750.406 | 20.006 | 1098.625 | 10.334 | 3685.875 | 49.863 |
| 5th | 21.03.2016 | 1758.912 | 80.280 | 1597.824 | 89.007 | 1037.324 | 63.751 | 3102.471 | 130.852 |
| | 22.03.2016 | 1734.040 | 26.741 | 1581.240 | 27.775 | 1011.840 | 20.291 | 3044.320 | 43.127 |
| | 23.03.2016 | 1709.417 | 4.821 | 1547.000 | 5.000 | 984.417 | 3.989 | 3029.750 | 10.117 |
| | 24.03.2016 | 1627.917 | 6.3365 | 1486.958 | 5.754591 | 962.875 | 3.836941 | 2900.750 | 14.31881 |
| | 29.03.2016 | 1708.485 | 144.4899 | 1567.152 | 167.7048 | 1013.667 | 124.2797 | 3043.091 | 238.2661 |

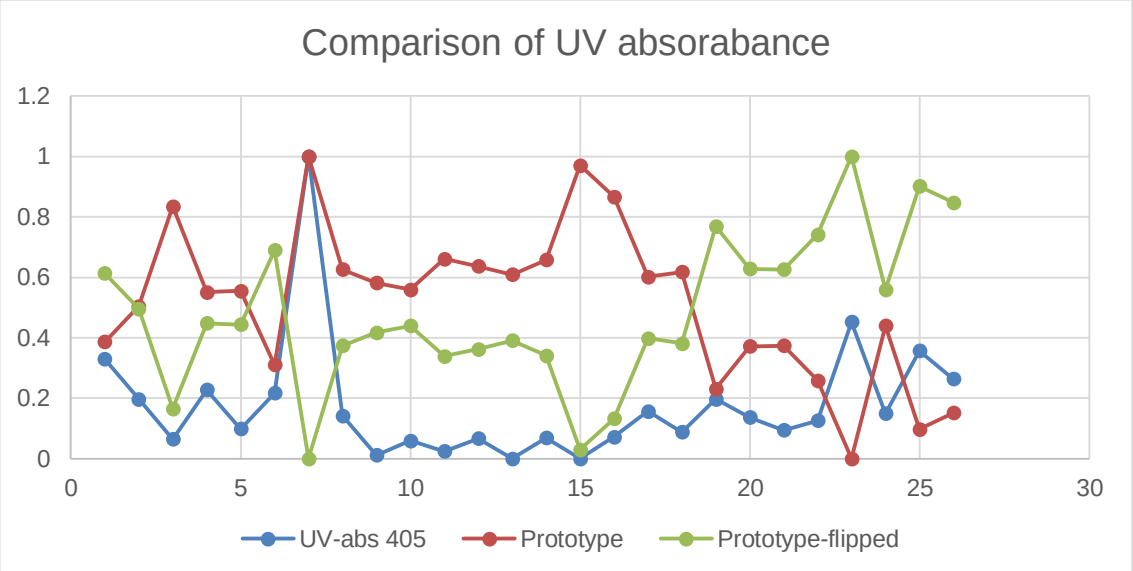
## Appendix 6. Online data from the mill

The raw data received from the company was processed and converted into the following format. Since a cleaning system was installed in the mill, data was restricted to the following selection.

| | Sample | | UV-abs (bytes) | | IR-abs (bytes) | | IR-sct (bytes) | |
|---|---|---|---|---|---|---|---|---|
| Dispatch | Date | Time | Average | Accuracy | Average | Accuracy | Average | Accuracy |
| 3rd | 29.02 | 7:40 | 2512.75 | 133.22 | 20944.75 | 179.93 | 1191.50 | 114.07 |
| | 1.03 | 7:30 | 2335.75 | 168.12 | 20470.00 | 264.59 | 1272.50 | 46.71 |
| | 2.03 | 7:45 | 2735.75 | 242.11 | 18166.50 | 414.84 | 1185.75 | 172.75 |
| | 3.03 | 7:45 | 2625.50 | 311.56 | 17088.50 | 858.10 | 1184.25 | 132.84 |
| | 4.03 | 7:03 | 2702.75 | 504.08 | 17132.50 | 266.26 | 1319.25 | 84.28 |
| 4th | 15.03 | 7:45 | 2338.75 | 262.61 | 15790.75 | 521.62 | 897.75 | 196.51 |
| | 16.03 | 7:45 | 2509.00 | 84.17 | 14029.75 | 217.14 | 994.50 | 50.55 |
| | 17.03 | 7:38 | 2577.00 | 90.18 | 15133.75 | 100.72 | 1163.25 | 15.61 |
| | 18.03 | 7:37 | 2368.75 | 22.25 | 15131.25 | 117.76 | 1052.25 | 59.47 |
| 5th | 21.03 | 7:35 | 3027.75 | 789.11 | 13900.75 | 168.71 | 961.00 | 385.83 |
| | 22.03 | 7:35 | 2339.25 | 158.40 | 13987.75 | 286.23 | 996.50 | 242.21 |
| | 23.03 | 7:37 | 2337.50 | 72.36 | 13676.75 | 51.62 | 1023.25 | 77.06 |
| | 24.03 | 6:23 | 2308.75 | 191.01 | 12411.00 | 231.11 | 945.50 | 104.07 |
| | 29.03 | 7:45 | 3283.75 | 160.63 | 6990.00 | 44.81 | 637.75 | 25.93 |

## Appendix 7. UV-abs comparison between lab device and prototype

This comparison includes all samples analyzed for this purpose.



## Appendix 8. Quality certificate, LCK514 (100-2000 mg/l COD)

Quality certificate
Technical data for Validation of LCK514 (100-2000 mg/l COD)

### Quality certificate

Technical data for cuvette test LCK514

| | |
|---|---|
| Sensitivity | 0.0005 Abs./(mg/l) |
| Ordinate intersect | 0.062 Abs. |
| Residual standard deviation | 0.0017 Abs. |
| Method variation coefficient | 0.33 % |
| Method standard deviation | 3.5 mg/l |
| Confidence intervall (95%) | ± 8.7 mg/l |

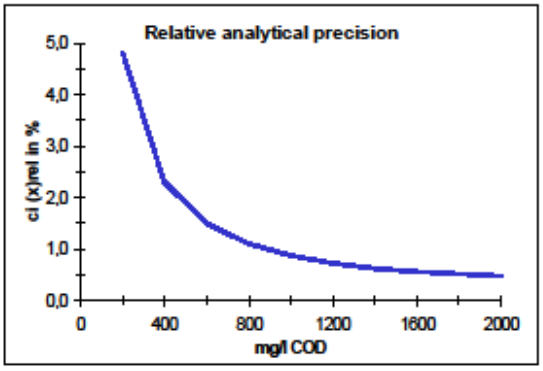
The technical data for cuvette test LCK514 were determined in conformity with ISO 8466-1 and DIN 38402 A51 „Calibration of analysis methods".

The series of the smallest and largest calibration standards exhibit normal distribution and are outlier- and trend-free.
The calibration gives a linear function.

Technical data in conformity with DIN 32645

| | |
|---|---|
| Detection limit | 4.6 mg/l |
| Quantitation limit | 13.7 mg/l |

The detection and the quantitation limits were determined in conformity with DIN 32645.




| Result | Confidence intervall (95%) |
|---|---|
| 400 mg/l | ± 9.3 mg/l |
| 800 mg/l | ± 8.8 mg/l |
| 1200 mg/l | ± 8.7 mg/l |
| 1600 mg/l | ± 9.0 mg/l |
| 2000 mg/l | ± 9.6 mg/l |

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## Appendix 9. Python codes programmed to run the prototype

Python codes used to run the prototype is attached in the following screen shots.

```
#!/usr/bin/python
#-*-coding: utf-8-*-

from Tkinter import *
import serial, time, datetime
import httplib, urllib
import sys
import ftplib
import re
import pylab
import matplotlib.pyplot as plt
import matplotlib.gridspec as gridspec

plt.ion()

start = time.time()

port = serial.Serial('/dev/ttyAMA0', 115200, timeout = 2) #portin lukuparametrit: portti, baudinopeus, timeout

port.flushInput()

x = 0

count = 0

x_data = []

y_data = []

y1_data = []
```

```
y2_data = []

y3_data = []

c_data = []

r_data = []

g_data = []

b_data = []

w_data = []

fname_str = ""

meascount = 0


def writetofile(logdata):
        global meascount

        meascount +=1

        if(meascount==1):
                filetowrite()

        if(meascount > 4500):
                meascount = 0
                reset_graph()
```

```
63
64          f = open(fname_str, 'a')
65          f.write(logdata)
66          f.closed
67
68  def filetowrite():
69
70          global fname_str
71
72          ts = time.time()
73          fname = datetime.datetime.fromtimestamp(ts).strftime('%Y-%m-%d %H-%M-%S')
74          fname_str = '/home/pi/Desktop/{0}.txt'.format(fname)
75
76
77  def parsedata():
78          datavec = []
79          data = port.readline().rstrip()
80          data_ = data.split()
81          data_1 = data_[0].split(":")
82          datavec.append(data_1[0])
83          datavec.append(int(data_1[1],16))
84
85          for n in range(1, len(data_)):
86                  datavec.append(int(data_[n],16))
87
88          return datavec
89
90
91  def reset_graph():
92          global x_data, y_data, y1_data, y2_data, y3_data, c_data, r_data, g_data, b_data, w_data, x, count
93          x_data = []
```

```
94            y_data = []
95            y1_data = []
96            y2_data = []
97            y3_data = []
98            c_data = []
99            r_data = []
100           g_data = []
101           b_data = []
102           w_data = []
103           x = 0
104           count = 0
105
106
107
108 def draw_ALL():
109     global x_data, y_data, y1_data, y2_data, y3_data, c_data, r_data, g_data, b_data, w_data
110
111     plt.figure(1)
112
113     plt.subplot2grid((4,2),(0,0))
114     plt.plot(x_data,y1_data, color = 'r')
115     plt.title('UV-abs')
116     plt.xticks([])
117
118     plt.subplot2grid((4,2),(0,1))
119     plt.plot(x_data,r_data, color = 'r')
120     plt.title('Color-R')
121     plt.xticks([])
122
123     plt.subplot2grid((4,2),(1,0))
124     plt.plot(x_data,y2_data, color = 'g')
```

```
125         plt.title('IR-scatter')
126         plt.xticks([])
127 
128         plt.subplot2grid((4,2),(1,1))
129         plt.plot(x_data,g_data, color = 'g')
130         plt.title('Color-G')
131         plt.xticks([])
132 
133         plt.subplot2grid((4,2),(2,0))
134         plt.plot(x_data,y3_data, color = 'b')
135         plt.title('IR-abs')
136         plt.xticks([])
137 
138         plt.subplot2grid((4,2),(2,1))
139         plt.plot(x_data,b_data, color = 'b')
140         plt.title('Color-B')
141         plt.xticks([])
142 
143         plt.subplot2grid((4,2),(3,0))
144         plt.plot(x_data,c_data, color = 'y')
145         plt.title('Conductivity')
146 
147         plt.subplot2grid((4,2),(3,1))
148         plt.plot(x_data,w_data, color = 'y')
149         plt.title('Color-W')
150 
151 
152         plt.tight_layout()
153         plt.draw()
154         plt.show()
155         master.after(100, draw_ALL)
```

```
157 #29 = conductivity = y3_data
158 #34 IR Scatter
159 #42 IR ABS
160 #50 UV ABS
161 
162 def data_organize():
163 
164         datavec = []
165 
166         Index = 0
167 
168         rowReady = False
169 
170         while rowReady==False:
171 
172                 data = parsedata()
173 
174                 rowIndex = data[0]
175 
176                 if(rowIndex=="0"):
177                         Index = 0
178                 if(rowIndex=="1"):
179                         Index = 9
180                 if(rowIndex=="2"):
181                         Index = 18
182                 if(rowIndex=="3"):
183                         Index = 27
184                 if(rowIndex=="4"):
185                         Index = 36
186                 if(rowIndex=="5"):
187                         Index = 45
```

```
                if(rowIndex=="6"):
                        Index = 54
                if(rowIndex=="7"):
                        Index = 63
                if(rowIndex=="8"):
                        Index = 72
                if(rowIndex=="L"):
                        Index = 81
                if(rowIndex=="9"):
                        Index = 90

                # print(Index)

                for n in range(1, len(data)):
                        datavec.insert((n + Index), data[n])

                if(Index==90):
                        rowReady = True

        #           datavec.append(datetime.datetime.fromtimestamp(time.time()).strftime('%Y-%m-%d %H-%M-%S'))

        return datavec

def measRecord():

 #29 = conductivity = y3_data
 #34 IR Scatter
 #42 IR ABS
 #50 UV ABS

        s = ","

        data = data_organize()

        global x_data, y_data,  y1_data, y2_data, y3_data, c_data, r_data, g_data, b_data, w_data, count, x

        count +=1

        if(count > 3):

                x = x+1

                y_data.append(data[1])

                y1_data.append(data[50]) # UV-abs

                y2_data.append(data[34]) # IR-scatter

                y3_data.append(data[42]) # IR-abs

                c_data.append(data[29]) # Conductivity (resistance)

                r_data.append(data[72]) # R

                g_data.append(data[73]) # G

                b_data.append(data[74]) # B

                w_data.append(data[75]) # W

                x_data.append(x)
```

```
250             data_string = s.join(str(e) for e in data)
251
252             ts = time.time()
253             ts_ = datetime.datetime.fromtimestamp(ts).strftime('%Y-%m-%d %H-%M-%S')
254
255             writetofile(ts_ + "," + data_string + "\n")
256
257             b.config(text="Recording")
258
259             master.after(5, measRecord)
260
261
262     master = Tk()
263     master.wm_title('DATALOG')
264
265     b = Label(master, text = "Not recording")
266     b.pack()
267
268     c = Button(master, width = 20, text="START RECORDING", command=measRecord)
269     c.pack()
270
271     d = Button(master, width = 20, text="STOP PROGRAM", command=master.destroy)
272     d.pack()
273
274     draw_ALL()
275
276     master.mainloop()
277
278
279
280
```